



Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Travis Air Force Base, Fairfield, California Using a Risk-Based Approach

Authors:

Walt W. McNab, Jr.
Brendan P. Dooher
David W. Rice
Michael C. Kavanaugh*
Stephen J. Cullen**
Lorne G. Everett**
William E. Kastenberg***
Matthew C. Small****
Paul C. Johnson*****

Submitted to the Air Force Center for Environmental Excellence
Environmental Restoration Directorate
Technology Transfer Division, Brooks Air Force Base, Texas

June 1997

*Malcolm Pirnie, Inc., Oakland
**University of California, Santa Barbara
***University of California, Berkeley
****U.S. Environmental Protection Agency, San Francisco, California
*****Arizona State University, Tempe



Environmental Protection Department
Environmental Restoration Program and Division

Assessment of Appropriate Fuel Hydrocarbon Cleanup Strategies for Travis Air Force Base, Fairfield, California Using a Risk-Based Approach

Authors:

**Walt W. McNab, Jr.
Brendan P. Dooher
David W. Rice
Michael C. Kavanaugh*
Stephen J. Cullen**
Lorne G. Everett**
William E. Kastenberg***
Matthew C. Small****
Paul C. Johnson*******

**Submitted to the Air Force Center for Environmental Excellence
Environmental Restoration Directorate
Technology Transfer Division, Brooks Air Force Base, Texas**

June 1997

***Malcolm Pirnie, Inc., Oakland
**University of California, Santa Barbara
***University of California, Berkeley
****U.S. Environmental Protection Agency, San Francisco, California
*****Arizona State University, Tempe**

**Environmental Protection Department
Environmental Restoration Division**

Acknowledgements

This study is part of the DoD Petroleum Hydrocarbon Demonstration Program (PHCDP). Funding for this work was provided by the U.S. Air Force Center for Environmental Excellence (AFCEE), Environmental Restoration Directorate, Technology Transfer Division (ERT) at Brooks Air Force Base, Texas. Marty Faile, Division Chief, and Patrick Haas, AFCEE/ERT Point of Contact, have been very supportive, and have provided the necessary Air Force guidance and backing for this effort. Charles Lee, of the AFCEE Regional Compliance Office in San Francisco, has been the champion of this effort within the military community, and has worked tirelessly to create and sustain this Program. His Risk Execution Strategy for Clean-Up of the Environment (RESCUE) has been the guiding vision for PHCDP and the LUFT demonstrations at military bases in California.

A number of dedicated individuals have contributed to the preparation of this report. The authors would like to thank the following individuals for their dedication, expertise, and hard work:

H. Barnes
D. Bishop
W. Day
R. Depue
R. Ragaini
J. Wharton

Table of Contents

| | | |
|--------|--|----|
| 1. | Program Overview..... | i |
| 1.1. | Background..... | 1 |
| 1.1.1. | The Use of Natural Attenuation..... | 1 |
| 1.2.1. | Risk-Based Corrective Action..... | 2 |
| 1.2. | LUFT Demonstration Program..... | 3 |
| 2. | Site Overview | 5 |
| 2.1. | Background..... | 5 |
| 2.2. | Site Conceptual Model | 5 |
| 3. | Risk Analyses..... | 6 |
| 3.1. | Sources..... | 6 |
| 3.1.1. | Primary Source(s)..... | 6 |
| 3.1.2. | Secondary Source(s)..... | 7 |
| 3.2. | Exposure Pathways..... | 7 |
| 3.2.1. | Review of Site Transport and Fate Modeling | 8 |
| 3.2.2. | Rate of Bioattenuation..... | 8 |
| 3.2.3. | Uncertainty Analysis of Passive Bioremediation | 9 |
| 3.2.4. | MTBE Groundwater Exposure Pathway | 11 |
| 3.2.5. | Inhalation Pathways..... | 12 |
| 3.3. | Receptors | 12 |
| 3.3.1. | Human Health Receptors—Groundwater | 12 |
| 3.3.2. | Human Health Receptors—Vapor..... | 12 |
| 3.3.3. | Ecological Risk Receptors..... | 12 |
| 4. | Summary and Recommendations..... | 12 |
| 5. | References..... | 14 |

Figures

| | | |
|-----------|---|----|
| Figure 1. | TMB ratio analysis at NSGS, Travis AFB..... | 10 |
|-----------|---|----|

Appendices

| | |
|--|------------|
| Appendix A. Travis Air Force Base Site Assessment Evaluation Letter..... | A-1 |
| Appendix B. Uncertainty Analyses of Fuel Hydrocarbon Bioattenuation Signatures in Groundwater by Probabilistic Modeling..... | B-1 |
| Appendix C. Uncertainty Analyses and Risk Assessment of Volatile Fuel Hydrocarbon Flux in the Vadose Zone Using Probabilistic Forecasts..... | C-1 |
| Attachment A. A Critique of a Steady-State Analytical Method for Estimating Contaminant Degradation Rates..... | Attach A-1 |

1. Program Overview

1.1. Background

In June 1994, the State Water Resource Control Board (SWRCB) contracted with the Lawrence Livermore National Laboratory/University of California (LLNL/UC) Leaking Underground Fuel Tank (LUFT) Team to study the cleanup of LUFTs in California. The study consisted of data collection and analysis from LUFT cases and a review of other studies on LUFT cleanups. Two final reports were submitted to the SWRCB in October and November 1995. These reports were entitled: *Recommendations To Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)*, and *California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis*.

Prior to submittal, both LLNL/UC reports were subjected to extensive internal peer review within the LLNL, as well as within each of the four UC campuses involved: UC Berkeley, UC Santa Barbara, UC Davis, and UC Los Angeles. The U.S. Environmental Protection Agency (EPA) has reviewed both LLNL/UC reports and issued a fact sheet supporting the findings and recommendations. Both reports have received national attention and have been extensively reviewed by many interested parties.

Data were collected primarily from the alluvial geologic settings typical of the San Francisco Bay Area, Los Angeles Basin, and the Central Valley. These data represent California's highly populated areas where most gas stations are found and most LUFT releases occur. Study results can be applied to similar settings throughout California. The length of dissolved benzene plumes in groundwater at LUFT releases were evaluated over time to determine how plumes behave. Over 1,200 LUFT cases were evaluated. Benzene was analyzed because it is the human carcinogen of greatest concern in fuel. It is relatively soluble in water, and cleanup standards are generally tied to benzene concentrations.

Ninety percent of the dissolved benzene plumes were less than 260 ft in length. Most of these plumes were either stable or shrinking in length. Seventy percent of the plumes in the study sites were found in shallow groundwater, less than 25 ft below the ground surface.

1.1.1. The Use of Natural Attenuation

The study concluded that with rare exceptions, petroleum fuel releases will naturally degrade (passively bioremediate) in California's subsurface environments. Passive bioremediation can control groundwater contamination in two distinct ways. First, passive bioremediation substantially lowers the risk posed to downgradient risk receptors through plume stabilization¹. Second, passive bioremediation actively destroys fuel hydrocarbon mass in the subsurface, leading to remediation of contamination over time (e.g., eventual decline and depletion of the dissolved hydrocarbon plume). From a risk management viewpoint, the stabilization of the dissolved plume is the most important contribution of passive bioremediation.

The use of passive bioremediation still requires site characterization and an assessment of potential risks. The need for active source removal must also be addressed on a site-by-site basis. Source removal includes removing leaking tanks and lines, and removing free product and

¹Even in the presence of a continuous constant source of fuel hydrocarbons (e.g., dissolution of residual free product components trapped in the soil matrix), a groundwater plume subject to passive bioremediation will reach a steady-state condition in which plume length becomes stable. This will occur when the rate of hydrocarbon influx from dissolution of the residual free product source is balanced by the rate of mass loss via passive bioremediation, integrated across the entire spatial extent of the plume.

petroleum fuel saturated soil, as much as economically and technically feasible. Although active source removal will contribute to higher rates of contaminant remediation in some instances, it will not diminish the risk posed to downgradient risk receptors by a plume which has already stabilized as a result of passive biodegradation.

The role of passive bioremediation in controlling the behavior of dissolved hydrocarbon plumes may be evaluated through both primary and secondary field evidence. Primary evidence includes quantitative evaluation of plume stability or plume shrinkage based upon trends in historical groundwater data. Secondary evidence includes indirect indicators of passive bioremediation, such as variations in key geochemical parameters (dissolved oxygen, nitrate, sulfate, iron, manganese, methane, alkalinity/carbon dioxide, Eh, pH) between measurements in fuel hydrocarbon-impacted areas and background. Although primary evidence of plume stability or decline generally provides the strongest arguments to support natural attenuation at a given site, such evidence may not be available because adequate historical groundwater monitoring may not exist. In these cases, short-term monitoring data, in conjunction with modeling where appropriate, may support a hypothesis for the occurrence of passive bioremediation if supported by secondary lines of evidence. Consequently, means for assessing the role of natural attenuation in controlling risk by secondary lines of evidence are to be more fully explored at such sites.

1.1.2. Risk-Based Corrective Action

The LLNL/UC recommendations report also concluded that risk-based corrective action (RBCA) provides a framework to link cleanup decisions to risk. For a risk to exist, there must be a source of a hazard, a receptor, and a pathway that connects the two. All three factors must be addressed to determine whether a LUFT release poses a risk to human health, safety, or the environment. If the source, pathway, or receptor are at all times absent, there is, by definition, no risk. The distinction between sources, pathways, and receptors may be context-dependent in many cases and therefore must be carefully defined. For purposes of the present assessment, definitions of these terms are developed by working backward from the receptor to the source:

Receptor: Human or ecological risk receptors which may potentially be subject to damage by long-term exposure to hydrocarbons via ingestion, inhalation, or absorption. This definition also specifically includes water supply wells because it must be assumed that humans will be ingesting the water from these wells.

Pathways: Physical migration routes of contaminants from sources to risk receptors. This definition specifically includes the groundwater environment downgradient of the source which provides a medium through which dissolved contaminants may migrate to water supply wells, as well as to surface water bodies which may serve as ecological risk receptors. The definition also includes the vadose zone in the immediate vicinity of the source, where vapor migration routes to nearby human receptors may exist.

Sources: Points of entry of contaminants into possible exposure pathways. In the case of hydrocarbon releases associated with LUFT sites, separate-phase hydrocarbon product which can either dissolve into the aqueous phase or volatilize into the gaseous phase constitutes a source. Primary sources will include underground tanks and associated piping; secondary sources will include any separate-phase hydrocarbon free product material residing within sediment pores.

From a mathematical viewpoint, sources and receptors represent boundary conditions for the problem of interest (influx and outflux, respectively); pathways represent the problem domain. Thus, in some special situations, the dissolved plume in groundwater may represent a source, such as in the case of Henry's law partitioning of contaminants from the aqueous phase into the gaseous phase. On the other hand, hydrocarbons which have adsorbed onto sediment surfaces from the aqueous phase cannot be regarded as potential sources in most situations according to this definition, but rather exist as part of the pathway.

Risk characterization is defined as an information synthesis and summary about a potentially hazardous situation that addresses the needs and interests of decision makers and of interested and affected parties. Risk characterization is a prelude to cleanup decision making and depends on an iterative, analytic, and deliberative process. This process attempts to gather all relevant data so the decision makers may then choose the best risk-management approach. If the risk of affecting receptors (humans or ecosystems) is low, then the following risk management strategy is appropriate and cost effective: 1) perform primary source removal (i.e., remove and upgrade leaking underground tanks and lines) and, 2) use passive bioremediation at low-risk sites, supported by monitoring as appropriate.

1.2. LUFT Demonstration Program

One of the important recommendations of this study was to identify a series of LUFT demonstration sites and to form a panel of experts made up of scientific professionals from universities, private industry, and Federal and State regulatory agencies. This panel would provide professional interpretations and recommendations regarding LUFT evaluations and closures at demonstration sites.

As a result of this recommendation, ten Department of Defense (DoD) sites were selected. Site selection was coordinated through the California Military Environmental Coordination Committee (CMECC) Water Process Action Team (PAT). Sites were selected to represent each branch of the military services with bases in California, as well as a number of Regional Water Quality Control Boards (RWQCB) and the diverse hydrogeologic settings in California where fuel hydrocarbon contaminant (FHC) cleanup problems occur. The sites selected and their corresponding RWQCB region are:

- Army Presidio at San Francisco, San Francisco RWQCB.
- Barstow Marine Corps Logistic Center, Lahontan RWQCB.
- Camp Pendleton Marine Corps Base, San Diego RWQCB.
- Castle Air Force Base, Central Valley RWQCB.
- China Lake Naval Weapons Center, Lahontan RWQCB.
- El Toro Marine Corps Air Station, Santa Ana RWQCB.
- George Air Force Base, Lahontan RWQCB.
- Port Hueneme Naval Construction Battalion Center, Los Angeles RWQCB.
- Travis Air Force Base, San Francisco RWQCB.
- Vandenberg Air Force Base, Central Coast RWQCB.

The Expert Committee (EC) selected to evaluate the selected demonstration sites are:

- Mr. David W. Rice, LLNL, Environmental Scientist; Project Director SWRCB LUFT Re-evaluation Project; LLNL/UC LUFT Team member; DoD FHC Demonstration Program Coordinator.
- Dr. Walt McNab, LLNL, Hydrogeochemist, with expertise in the evaluation of passive bioremediation processes.
- Dr. William E. Kastenberg, UC, Berkeley, Professor and Chairman, Department of Nuclear Engineering; member of LLNL/UC LUFT Team, with expertise in environmental decision making and decision analysis processes.

- Dr. Lorne Everett, UC, Santa Barbara, Hydrogeologist; head of the Vadose Zone Research Laboratory and member of LLNL/UC LUFT Team, with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Stephen Cullen, UC, Santa Barbara, Hydrogeologist; member of LLNL/UC LUFT Team with expertise in vadose zone FHC transport mechanisms and passive bioremediation processes.
- Dr. Paul Johnson, Arizona State University, Chemical Engineer; primary author of *American Society for Testing and Materials (ASTM) RBCA* guidance, with expertise in chemical fate and transport.
- Dr. Michael Kavanaugh, Chairman, National Research Council Alternatives for Groundwater Cleanup Committee; Principal and Environmental Engineer, Malcolm Pirnie, Inc., with expertise in evaluation of groundwater remediation alternatives and environmental decision making processes.
- Mr. Matthew Small, U.S. EPA Region IX, Hydrogeologist; Co-Chairman of U.S. EPA Remediation by Natural Attenuation Committee, with expertise in risk-based corrective action and passive bioremediation.

The demonstration program process can be summarized in the following nine steps:

- Step 1: Site scoping meeting with site staff, regulators, and EC staff representatives. Develop and discuss site conceptual model. Identify and discuss pathways and receptors of concern.
- Step 2: RBCA training for DoD Petroleum Hydrocarbon Cleanup Demonstration Program (PHCDP) participants.
- Step 3: Site staff and contractors prepare the data package. EC staff reviews available data and identifies data gaps needed to apply RBCA approach.
- Step 4: EC visits site and receives briefing, on site characterization, conceptual model, and pathways and receptors of concern. Site tour is included in this briefing. Following EC's visit, a site characterization report is prepared by the EC containing recommendations for further data collection, if needed.
- Step 5: EC staff applies RBCA approach to the site using best available data.
- Step 6: EC staff evaluates the natural attenuation potential for the site using best available data. An estimate of the time to clean up and the uncertainty associated with this estimate will be made. Sampling and monitoring procedures to support intrinsic bioremediation for the site will be identified.
- Step 7: Based on the concept of applied source, pathways, and receptors as to potential hazards, site specific findings regarding natural attenuation potential, and discussion with regulators, the EC shall provide its recommendations for an appropriate risk-management strategy at the site and the set of actions needed to achieve site closure. The EC will present its recommendations at an appropriate forum.
- Step 8: The EC will provide a DoD PHCDP overall evaluation comparing the effectiveness of CalRBCA at each site in the program. An estimation of the cost savings using the CalRBCA protocol will be compared to baseline approaches. An estimation of the value of the remediated water will be made.

- Step 9: The EC Staff will produce a DoD *Risk Execution Strategy for Clean-Up* of the Environment (RESCUE) implementation guide and accompanying procedures manual (Phase I, Petroleum) that can be used in California and in other states by military bases.

2. Site Overview

2.1. Background

Travis Air Force Base is located near the town of Fairfield, California. The North and South Gas Stations (NSGS) site at Travis AFB consists of two Base Exchange gasoline service stations, separated by a road running east-west. Both stations remain in current use. Land use immediately adjacent to the NSGS site consists of parking areas and housing dormitories. In the local vicinity of Travis AFB, primary land use is agricultural with some light industry.

Four underground storage tanks (USTs) were installed at the South Gas Station in 1960, and two more were installed in 1974. Three underground storage tanks were installed at the North Gas Station in 1965. Leaks from tanks at piping were discovered at both stations in 1988 (Weston, 1991). Following replacement of tanks and repairs to piping, remedial investigations were initiated to determine the extent of subsurface contamination. Minor quantities of free product have been noted in wells immediately adjacent to the tank pits, and groundwater contamination by dissolved BTEX has been noted several hundred feet in the downgradient direction. Methyl tertiary butyl ether (MTBE) has been detected in low concentrations (up to 3 parts per million [ppm]) in three monitoring wells in the vicinity of the tank locations. However, these detections do not appear to reflect any continuing releases from the existing tank/piping system and will likely disperse long before significant migration could occur.

As part of the site remedial investigation (Parsons, 1996) and a later treatability study (Parsons, 1996), the potential for natural attenuation of contaminants at the NSGS site has been evaluated. These studies concluded that the site groundwater has a high capacity to passively bioremediate the BTEX contaminants.

2.2. Site Conceptual Model

The subsurface environment at the NSGS site, and Travis AFB, in general consists of unconsolidated clays, silts, sands, and gravels typical of an alluvial setting. A surficial clay layer, approximately 10 to 15 feet in thickness, underlies the site and acts as an aquitard to underlying sands and silt. Site investigations have shown that soil concentrations of FHCs are highest along the interface between the clay and the coarser sediments. Underlying the sand and silt material at a depth of 20 to 40 feet below ground surface is a consolidated, weathered shale unit suspected as being the Nortonville Shale. Due to the very low permeabilities typically associated with shales, it is suspected that this unit acts as a lower confining layer for the alluvial aquifer. Vertical potentiometric differences indicate that any vertical flow may be expected to occur in the upward direction and thus not into the shale.

Groundwater at the NSGS site is typically encountered at the surficial clay-silt/sand interface, although the potentiometric surface often rises above this interface as indicated by water levels in monitoring wells. Water levels in the area have been found to respond significantly to precipitation, with average annual fluctuations on the order of 2 to 3.5 ft (Weston, 1991). Hydraulic conductivity has been estimated in several wells in the NSGS area based on the results of pumping tests as well as slug tests. Values generally range from 4×10^{-4} cm/s to 8×10^{-3}

cm/s. Hydraulic gradient, as estimated from water levels measured in NSGS area wells, has been found to be on the order of 0.002 and is in the general south-southeast direction. These values, taken with effective porosities associated with alluvial materials, suggest mean flow velocities on the order of 40 ft per year.

The spatial extent of BTEX/FHC concentrations in groundwater underlying the NSGS site appears to be well characterized, with total BTEX measured in 14 of 29 monitoring wells in concentrations ranging from 1.0 part-per-billion (ppb) up to 67,000 ppb (August/September 1995 sampling round, Parson Engineering Science, 1996). The dissolved BTEX plume extends approximately 600 ft downgradient of the North Gas Station site (as defined by the 10-ppb contour), or approximately 380 ft downgradient of the South Gas Station site. The total observed plume length is significantly longer than the majority of plume lengths observed in the study of Rice et al. (1995), falling above the 90th-percentile of approximately 340 ft. However, it is likely that the presence of two separate sources contributes to this effect by creating a co-mingled plume.

Long-term historical trends in groundwater data are unavailable, as sampling rounds have occurred only from 1994 through 1996. As a result, convincing primary evidence directly supporting stability or decline in the BTEX/FHC plume does not yet exist. However, geochemical indicators of bioattenuation provide secondary evidence that is strongly indicative of passive bioremediation at the site.

A review of the adequacy of the site conceptual model was presented to Travis AFB in a letter dated September 20, 1996 (Appendix A).

3. Risk Analyses

3.1. Sources

3.1.1. Primary Source(s)

FHCs are present in the subsurface at the NSGS site as a result of leaks from USTs and pipelines at both gas stations (both in operation since the 1960s). The total release volume is not well-bounded; inventory records indicated a loss of at least 3,800 gallons of unleaded gasoline at the South Gas Station between August and October 1988. The three USTs at the North Gas Station were replaced with double-walled tanks in 1988. Contaminated soil associated with the primary source(s) was removed to approximately 20 ft below ground surface. A leaking pipeline at the South Gas Station was excavated and repaired in 1994. After additional investigations in 1989 and 1990 indicated that gasoline contamination had spread outside the tank pit areas into nearby groundwater, all six USTs and piping at the South Gas Station were replaced. One of the removed tanks had visible holes up to 0.5 inches in diameter. During these removal activities, 10,000 gallons of groundwater and 1,700 yd³ of contaminated soil, to a depth of 16 ft below ground surface, were removed.

3.1.2. Secondary Source(s)

Secondary contamination sources consist of potential residual free product lenses or ganglia on or above the water table. The extent of residual free product at the NSGS appears to be limited in extent to areas near the UST locations and associated piping. Historically, free product has been observed in only three monitoring wells: MW-135 (North Gas Station) and MW-138 and MW-141 (South Gas Station). During a January 1996 inspection, no free product was observed in any of these three wells. It is possible that excavation and groundwater extraction associated with UST and piping replacement removed a significant portion of the free product at the site. However,

small quantities of residual free product may still exist in the vadose zone or on the water table. No free product removal efforts are currently underway at the site.

3.2. Exposure Pathways

To pose a human health or ecological risk, the source of contaminants (e.g., residual NAPL) must be linked to receptors (e.g., water-supply wells) via pathways. Groundwater provides such a pathway through advective, dispersive, and diffusive transport of dissolved contaminants. However, passive bioremediation processes tend to limit the migration of dissolved hydrocarbons; the input of dissolved FHCs from residual sources is balanced by FHC loss integrated over the extent of the plume. This mass balance constraint is the likely explanation for the limited dissolved-phase plume lengths associated with majority of LUFT sites (Rice et al., 1995). Such a limitation of dissolved plume length implies that the groundwater pathway is often incomplete. Therefore, the problem of evaluating the groundwater exposure pathway is linked directly to an assessment of plume stability.

At the NSGS site, several lines of field evidence have been explored to assess the extent of passive bioremediation of the dissolved FHC plume. These include:

- Changes in concentrations of BTEX constituents over time and distance (Primary line of evidence).
- Changes in concentration ratios of BTEX components to those of presumed recalcitrant hydrocarbon tracers such as trimethyl- and tetramethylbenzene isomers (Secondary line of evidence).
- Analyses of geochemical indicators of passive bioremediation (e.g., dissolved oxygen, nitrate, sulfate, manganese, iron, bicarbonate alkalinity, methane, pH, Eh) in groundwater (Secondary line of evidence).

Primary (direct) evidence of passive bioremediation is weak because insufficient historical monitoring data, e.g., only two sampling events, separated by approximately one year, exists to convincingly demonstrate plume stability or retreat. The reliability of recalcitrant tracer analyses for providing convincing evidence of passive bioremediation is also unclear because of poor correlation of concentration ratios with distance (see discussion below). However, geochemical data do provide strong secondary evidence of significant passive bioremediation. Data collected from site monitoring wells indicate a number of electron acceptors are being utilized in mineralization reactions involving dissolved FHCs.

In the absence of historical monitoring data which convincingly demonstrate plume stability or plume decline, predictive modeling of plume behavior which directly incorporates analysis of secondary evidence can be used to assess plume stability. The likelihood that the plume has reached a steady-state condition may be evaluated in a quantitative manner using a conservative contaminant transport model (one that assumes a continuous source of contamination), probability distributions of the governing hydrogeological and hydrogeochemical parameters (based on site data and best professional judgment), and the length of time the source has been active. This approach is discussed further in Section 3.2.2 and in Appendix B.

An additional issue regarding groundwater migration pathways is the potential for vertical transport of dissolved FHCs into sediments beneath the underlying Nortonville Shale formation. Given the very low permeability values typically associated with shales, and the upward flow direction implied by the observed groundwater potential at the site, it appears that the possibility of significant migration of dissolved hydrocarbons into any underlying units is minimal. Even if downward-direction solute migration were to occur, such transport could probably only occur through fractures in the shale. In such cases, only localized point or line sources of low

concentration would be established in underlying units. Dissolved contaminants associated with such sources would be quickly subject to passive bioremediation or physical dispersion processes. Therefore, contamination of units underlying the Nortonville Shale at the NSGS site does not constitute a plausible exposure pathway at this site.

3.2.1. Review of Site Transport and Fate Modeling

To assess potential future behavior of the dissolved FHC plume at the NSGS site, a modeling study was undertaken using BIOPLUME II (Parsons Engineering Science, 1996). The BIOPLUME II modeling considered the combined effects of advective and dispersive transport, biodegradation limited by dissolved oxygen content, and biodegradation under anaerobic conditions using a first-order decay coefficient. Three source depletion scenarios were evaluated: gradual source weathering, engineered source reduction through bioslurping, and bioslurping combined with groundwater pump and treat. Sensitivities of model results to transmissivity, dissolved oxygen content, and the anaerobic decay coefficient were also evaluated.

For the natural source weathering scenario, BIOPLUME II modeling results suggest that the plume will continue to expand, reaching its maximum downgradient extent of 1,050 ft. beyond the August/September 1995 plume limit in 2027. Although the plume is predicted to decline after this point, significant BTEX concentrations were predicted to remain for an additional 50 to 100 years (Parsons Engineering Science, 1996). Under both engineered source removal scenarios, the plume is predicted to continue advancing some 700 to 800 ft beyond its present boundary before declining, with total BTEX concentrations falling below MCLs within 30 to 35 years.

It is our opinion that the BIOPLUME II modeling conducted for the NSGS site provides a reasonable framework in which to view the capacity of natural attenuation processes to control hydrocarbon plume movement and therefore affect the groundwater pathway. To enhance the credibility of the BIOPLUME II modeling, Parson addressed uncertainties in the governing hydrological and chemical parameters by using conservative estimates. Such an approach is warranted for the purposes of assessing risk in terms of potential impacts to downgradient risk receptors. However, we believe that the deterministic conservative modeling results may be too unrepresentative for the purposes of planning monitoring strategies to guard against further plume migration. In particular, the degradation rates estimated using the BIOPLUME II modeling may be too low.

3.2.2. Rate of Bioattenuation

The mean rate of passive bioremediation directly affects the risk pathway assessment by ultimately determining the stable plume length; shorter plume lengths clearly pose less of a probable risk to downgradient receptors than do longer plumes. Two methods were employed in the NSGS natural attenuation study to estimate a mean first-order decay rate for BTEX degradation at the NSGS site (Parsons Engineering Science, 1996). One method involved using the one-dimensional steady-state model of Buscheck and Alcantar (1995) to derive a decay coefficient based upon an idealized concentration distribution with distance. The second method involved normalizing BTEX concentrations by those of recalcitrant tracer compounds (e.g., trimethylbenzenes) as a function of distance from source(s). Both methods yielded anaerobic degradation rates of approximately $0.05\% \text{ day}^{-1}$. In our opinion, this estimated BTEX degradation rate may be too conservative. The reasons for this include:

1. Despite the widespread application of the method of Buscheck and Alcantar (1995) for estimating mean first-order decay rates, it is our opinion that the method is potentially misleading as applied at the NSGS site. A full discussion of the issues involved is presented in Attachment A.

2. The method of Buscheck and Alcantar (1995) assumes a steady-state plume; i.e., a plume in which the rate of FHC influx from a source is balanced by loss due to degradation, integrated across the extent of the plume. However, use of the estimated decay rate of $0.05\% \text{ day}^{-1}$ in the BIOPLUME II site model resulted in continued migration of the plume, doubling in downgradient extent over a period of approximately 30 years (even in the presence of diminishing source term). Thus, the decay rate estimated by the method of Buscheck and Alcantar (1995) is not consistent with a stable plume, a requirement for application of this rate estimation method.
3. The trimethylbenzene normalization procedure appears to be highly problematic. Our analysis of the concentration ratios of total BTEX to four trimethylbenzene isomers (1,3,5-TMB, 1,2,4-TMB, 1,2,3-TMB, 1,2,3,4-tetramethylbenzene) as a function of distance from the North Gas Station indicates that there is far too much scatter in the data (August/September, 1995 sampling round) to enable a good estimation of a mean rate constant. This analysis is presented on Figure 1.
4. Using a probabilistic modeling approach to simulate reactive transport of dissolved FHCs, the observed distribution of electron acceptors and other geochemical indicator data are better explained by higher degradation rates. This modeling approach is explained in Section 3.2.3 below and in Appendix B.
5. As noted in the natural attenuation report (Parsons Engineering Science, 1996), the estimated degradation rate constant is low compared to values obtained from other anaerobic sites with similar patterns of electron acceptor depletion.

3.2.3. Uncertainty Analysis of Passive Bioremediation

In many instances, it may not be possible to reliably extract a mean degradation rate for dissolved FHCs in groundwater, given uncertainties pertaining to the source term, dispersion, local variations in degradation rates, and so forth. A more robust approach may be to assume a range of possible degradation rates based on best professional judgment and incorporate these values into a general analysis of uncertainty using Monte Carlo techniques or similar methods.

A complete model of passive bioremediation of dissolved hydrocarbon should address not only changes in FHC concentrations over time and distance but should also seek to incorporate changes in geochemical indicator species concentrations as well. Even if simplifying assumptions concerning electron acceptor utilization are employed, such an approach for estimating passive bioremediation rates is much better constrained by data than a single-species (i.e., hydrocarbon-only) modeling approach. However, the site-specific hydrogeologic and groundwater chemical data required for such estimates are characterized by inherent uncertainties arising from both the heterogeneous nature of the subsurface environments and as artifacts of measurement techniques (e.g., the use of aquifer tests to interpret mean hydraulic conductivity). The integrated effects of

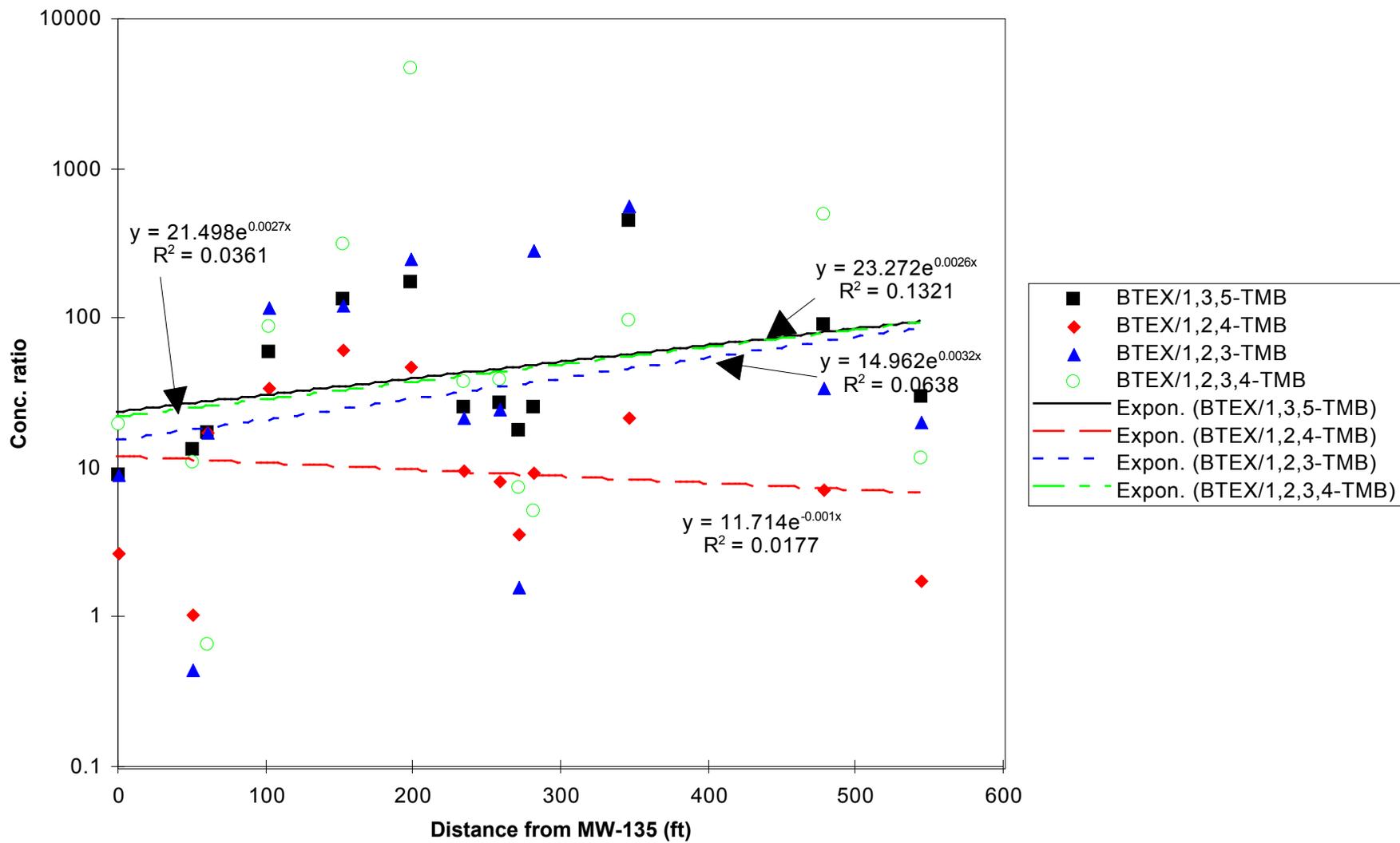


Figure 1. TMB ratio analysis at NSGS site, Travis AFB.

such uncertainties may compound the uncertainty in predictions generated by flow and transport models.

From a risk-based viewpoint, an understanding of the uncertainties associated with natural attenuation processes, and their capacity to limit plume migration, is of great importance in 1) quantifying the extent of bioattenuation, and 2) characterizing the degree of risk from further plume movement. As such, a modeling approach which integrates FHC degradation, the dynamic response of geochemical indicator species, and uncertainties in the pertinent hydrologic and geochemical data provides a useful alternative means for assessing present and future plume behavior. We have used a probabilistic screening model based on this approach as an independent means of evaluating how natural attenuation affects present and future BTEX plume behavior at the NSGS site. This model is based upon an analytical solution to the two-dimensional solute transport equation (Domenico, 1987), coupled with stoichiometric mass balance constraints on the sequential utilization of available electron acceptors. This particular model is conservative because it assumes a continuous line source as a boundary condition. A Monte Carlo simulation routine is used to generate multiple realizations of combinations of governing hydrogeologic and geochemical parameters which affect the behavior of the system. The probability distributions of these parameters were derived from site data supplemented by best professional judgment. The development of the model is formally presented in Appendix B.

Output from the Monte Carlo simulations consists of probability distribution functions for the concentrations of total BTEX, as well as those of various electron acceptors at individual monitoring well locations over time since assumed source activation (Appendix B). In general, forecast probability distributions of total BTEX, dissolved oxygen, nitrate, sulfate, iron, manganese, and alkalinity are consistent with observation (i.e., monitoring well data collected during the August/September 1995 sampling round) at the NSGS site. These results suggest that the probability distributions used as model assumptions are reasonable for the NSGS site. This includes a distribution of first-order degradation rates characterized by a mean value of $0.8\% \text{ day}^{-1}$, which is significantly larger than the conservative value used in the BIOPLUME II simulations. Hence, the BIOPLUME II modeling results may not represent site conditions in certain contexts, particularly when extrapolated forward to predict future plume behavior. Our calculations of future plume behavior, using the same governing parameter distributions which include the distribution of degradation rates about $0.8\% \text{ day}^{-1}$, suggest that the BTEX plume is likely to remain in the same state and position as present, assuming a continuous source.

3.2.4. MTBE Groundwater Exposure Pathway

MTBE was detected in three NSGS monitoring wells in November 1996. These include MW-135 at the North Gas Station (2,802 ppb), MW-138 at the South Gas Station (1,086 ppb), and MW-139 (39 ppb), approximately 100 ft. from MW-138. MTBE was not detected above 1 ppb in six other wells sampled in the area.

The source of the MTBE in the three wells is unknown. It is unlikely that it is a result of leaks from existing tanks or piping as extensive leak detection/prevention systems are now in place (Personal Communication, Wilford Day, January 1997). These include leak detection alarms and sump probes in continuous operation mode, annual precision testing of piping, mechanical leak detectors, etc. To date, no leaks have been noted. It is possible that MTBE was present in releases from the tanks prior to tank and pipeline repair activities. It is also possible that MTBE may have been introduced into the subsurface by a surface spill event. In either case, because MTBE has been detected in only three wells in the immediate vicinity of the tank locations, and because the concentrations are relatively low, it appears highly probable that it will disperse long before reaching the site boundary. Hence, no risk receptors are threatened by MTBE at the NSGS site.

3.2.5. Inhalation Pathways

At LUFT sites, the inhalation (vadose zone) pathway must be evaluated in addition to the ingestion (groundwater) pathway. Ignoring vadose zone potential for degradation and advective downward flux of the constituents due to recharge, a highly conservative one-dimensional diffusive flux model (infinite mass transfer coefficient at the surface) indicates that hydrocarbon vapors will be attenuated before reaching the nearby housing complex (see below), so the inhalation pathway is not completed. An inhalation pathway could exist at the gas station properties.

Calculations pertaining to vapor transport are presented in Appendix C.

3.3. Receptors

3.3.1. Human Health Receptors—Groundwater

With respect to contaminated groundwater, no human health receptors (i.e., water-supply well) have been identified within one mile of the NSGS site. To a very high confidence level (greater than 99%), this distance is well beyond the likely extent of a dissolved FHC plume (Rice et al., 1996) and the estimated stable plume length at the NSGS site.

3.3.2. Human Health Receptors—Vapor

Base residences exist in the vicinity of the North Gas Station, forming a semi-circle arc approximately 300 ft upgradient of the northern plume boundary. Air Force personnel and their families typically reside in these dwellings for periods of six months to two years. Although these residences do constitute theoretical vapor receptors, the distance from the source implies the exposure risk is low (Appendix C).

Mechanics and store clerks on duty at the two service stations also constitute risk receptors for hydrocarbon vapors. However, it is anticipated that any hydrocarbon vapor exposure associated with residual free product in the subsurface would be insignificant in comparison to everyday workplace exposure in such establishments. As such, risks to these personnel are more appropriately addressed under Occupational Safety and Hazards Administration (OSHA) jurisdiction.

3.3.3. Ecological Risk Receptors

No ecological risk receptors have been identified.

4. Summary and Recommendations

For a dissolved hydrocarbon plume to pose a risk to human health or to the local ecology, a source, pathway, and receptor must all simultaneously co-exist. The absence of any of these elements implies that there is no associated risk. At the NSGS site at Travis AFB, each of these elements has been assessed independently.

Sources. Leaking USTs and associated piping have been replaced; contaminated soil and groundwater were removed during excavation. Some residual free product may remain in the subsurface in the vicinity of the two gas station tank pits. This volume cannot be reliably quantified, but is probably very low.

MTBE has been detected at relatively low concentrations in three wells in the immediate vicinity of the tank locations. However, the MTBE does not appear to be associated with any continuing leaks and is likely to disperse without forming a hazard.

Pathways. Historical groundwater quality modeling at the NSGS site, consisting of two sampling rounds over a period of approximately one year, is insufficient to provide primary direct evidence of hydrocarbon plume stability or retreat. However, geochemical indicator data do provide clear secondary evidence of fuel hydrocarbon bioattenuation. Flow and transport modeling of the BTEX plume with the BIOPLUME II model suggests that the plume will eventually stabilize and then begin to decline. Further analyses suggests that the BIOPLUME II modeling results are probably overly conservative. As the plume is probably at or near a steady-state condition at present without engineered controls, the use of engineered product removal will not substantially reduce risk to any potential downgradient receptors.

In regard to vapor exposure, our calculations indicate that this pathway is incomplete, due primarily to the distance between the gas stations and nearby base housing and a fire station.

Receptors. Accounting for current local land use, it appears that there are no receptors at risk of detrimental impact by the dissolved hydrocarbons in the subsurface. Furthermore, because the hydrocarbon plume remains on Air Force property, institutional controls can be implemented to assure against hydrocarbon exposure risks associated with unanticipated land use or groundwater use activities. Potential vapor receptors do exist in the vicinity (base housing, fire station).

The need to meet beneficial use cleanup objectives must be considered as part of any risk management strategy at TAFB. When considering beneficial use impacts, groundwater itself becomes defined as a receptor. As such, plume stability is replaced by time-to-cleanup as the key technical issue. The conservative results of the BIOPLUME II modeling suggests that time-to-cleanup will be on the order of several decades. In the meantime, because the property is controlled by the U.S. Air Force, institutional controls will provide added protection of public health while beneficial use is being restored by passive bioremediation.

The risk associated with the hydrocarbon plume at the NSGS site at Travis AFB is minimal. Given this low risk, we believe that remediation by natural attenuation, as advocated by Travis AFB, will protect human health and the environment and is thus an acceptable means of remediation at the site. As a safeguard measure, we recommend that at least two existing wells located near the downgradient edge of the dissolved plume be chosen as sentry wells, and be monitored for BTEX components annually for two years to validate predicted plume stability. Although free product removal may increase the rate of contaminant mass removal as a supplement to that of natural attenuation, uncertainties involved in the source term complicate quantifying this benefit. Furthermore, given the plume stabilizing effect of natural attenuation, and the distance to potential downgradient risk receptors, there is no added benefit of engineered source removal in reducing risk.

5. References

- Buscheck, T. E., and C. M. Alcantar (1995), Regression Techniques and Analytical Solutions to Demonstrate Intrinsic Bioremediation, in *Proceedings of the 1995 Battelle International Symposium on In Situ and On-Site Bioreclamation*, April 1995.
- Decisioneering, Inc. (1996), *Crystal Ball: Forecasting and Risk Analysis for Spreadsheet Users*, Decisioneering, Inc., Aurora, Colorado, 1996.
- Domenico, P. A. (1987), An Analytical Model for Multidimensional Transport of a Decaying Contaminant Species, *Journal of Hydrology*, **91**, 49–58.
- Parsons Engineering Science, (1996), *Final Treatability Study to Evaluate Intrinsic Remediation at the North and South Gas Stations, Travis Air Force Base, California*. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas.
- Rice, D.W., B. P. Dooher, S. J. Cullen, L. G. Everett, W. E. Kastenberg, R. D. Grose, and M. A. Marino (1995), *Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks (LUFTs)*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-121762).
- Rice, D. W., R. D. Grose, J. C. Michaelsen, B. P. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. G. Everett, and M. A. Marino (1995), *California Leaking Underground Fuel Tank (LUFT) Historical Analyses*, Lawrence Livermore National Laboratory, Livermore, Calif. (UCRL-AR-122207).
- Roy F. Weston, Inc. (1991), *Stage 1 Draft Final RI/FS report, North and South Gas Stations, Travis Air Force Base*.

Appendix A

Travis Air Force Base Site Assessment Evaluation Letter



Lawrence Livermore National Laboratory

September 20, 1996

TO: Distribution

FROM: Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program Expert Committee

SUBJECT: Review of Travis Air Force Base Site Investigation

The Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program Expert Committee has reviewed the methods and findings of the site investigations conducted at the north and south gas stations (NSGS) at Travis Air Force Base (TAFB), located near Fairfield, California. These investigations have been conducted by Parsons Engineering Science, Inc. and others as part of an evaluation of remedial options for gasoline released at the NSGS sites. Included in this evaluation is a treatability study to evaluate the use of intrinsic remediation. This review of the site investigation includes our evaluation of the adequacy of the site risk characterization and conceptual model as a credible basis for applying risk-based corrective action (RBCA) to the site, emphasizing natural attenuation as a means of remediation to achieve site closure.

This letter represents the first of two deliverable documents as part of our overall assessment. It is intended solely as a brief review of the existing site data and risk characterization. Request for additional data collection and clarification needed to complete the site review are provided. Specifically, the review included:

- An assessment of site characterization and the contaminant distribution, based upon conformance with standard environmental investigation practices and sound scientific judgment;
- An assessment of bioattenuation potential, based upon presentation of multiple lines of evidence such as natural geochemical indicators and changes in plume composition over time;
- An assessment of risk characterization, based upon our judgment as to how significant uncertainties in risks posed to potential receptors have been characterized.

96-9/9-033hk

Site Description and History

The statement in the "Treatability Study to Evaluate Intrinsic Remediation at the North South Gas Stations", page 3-2, indicates "Recharge to groundwater through precipitation may also occur in locations upgradient of the site where the aquifer is unconfined". This suggests that, to some degree, the authors think that there is some contribution of direct vertical infiltration of precipitation water at the site. Is this the case? What is the evidence? Is there perched water above the confining zone? If it can be demonstrated that onsite precipitation is not contributing to the recharge, this removes a significant driving force for the movement of petroleum hydrocarbons left after excavation.

Past Subsurface Investigations and Remedial Actions

Treatability Study (TS) Geologic Cross-section A-A' (Figure 3.6) shows that engineered fill associated with the UST excavations extend from ground surface to 5.5' and 4.5' bgs at the south and north gas stations, respectively. Committee members did not feel comfortable with these depths of excavations. What were the dimensions of the tanks that came out of these small pits? Further explanation of the depth of excavations, materials used to backfill, and the exact nature of the surface completions is requested. It should be clearly indicated whether the excavation intersected groundwater at the site. If it has, as TS text pages 4-4 and 4-5 seem to indicate, then the possibility of recharge through the presumably coarse textured backfill becomes an issue.

Identification of Sources

The extent of the free product at the site is not well defined, but based on the benzene concentrations in groundwater at MW-138 and MW-210, the present extent of the free product appears to be modest. Historically, through 1995, two to four inches free product has been observed in MW-135 (North Gas Station) and MW - 138 and MW- 141 (South Gas Station). During January 1996, no free product was observed in these wells. While these sparse data are adequate for the application of risk based corrective action (RBCA) at the site, they force conservative estimates of free product extent.

The use of these conservative assumptions in place of further spatial constraints on the source will tend to yield long estimated times for cleanup using natural attenuation. If these estimates for source depletion and remediation through natural attenuation are unacceptable, there may be a cost advantage to constructing an additional boring between MW-210 and MW-138 to refine the estimated source mass.

Identification of Pathways

In our opinion, the distribution of contaminants at TAFB has been reasonably well characterized, except that there is no quantitative data presented for methyl tertiary butyl ether (MTBE), a gasoline additive that has been detected in groundwater at the site, but not quantified.

The information provided in the TS provides strong qualitative evidence of biodegradation of dissolved benzene, toluene, ethylbenzene, and xylene (BTEX)

contamination in shallow groundwater at the NSGS site. At issue is the stability of the plume. Using conservative estimates that tend to overestimate plume size, the Bioplume II model, as presented in the treatability study, predicts that the plume will stabilize about 1350 feet beyond the source area (MW-138). This distance is significantly longer than observed at leaking underground fuel tank (LUFT) sites in similar hydrogeologic settings within California. The LUFT historical case analysis currently being conducted by the State Water Resources Control Board indicates that among the 271 LUFT cases with best available data, the longest plume measured to a benzene concentration of one ppb was less than 800 feet. This difference appears to be due the continued presence of a source and the conservative assumptions that are made regarding the mass, dissolution and depletion of this source. At present the data available to evaluate plume stability are based on three closely spaced groundwater sampling events, July 1994, December 1994/January 1995, and August/September 1995. Additional sampling for BTEX will be needed to establish if the plume length and mass is increasing, stable, or decreasing with time. The potential for natural attenuation mechanisms to limit the extent of the dissolved FHC plume will be evaluated by the Expert Committee as part of the follow-on risk management report.

Parsons ES has assumed that the underlying Norton Shale forms an impermeable layer beneath the hydrocarbon-contaminated water-bearing unit. While this may be a reasonable assumption, the absence of vertical head gradients with respect to the water-bearing units beneath the shale has not been verified. During any additional groundwater sampling at the site, a vertical profile of groundwater contamination would validate the shallow nature of the NSGS plume. During this sampling, monitor wells selected for vertical gradient sampling should not be purged prior to sampling. MW-135 and MW-138 are appropriately screened and we suggest that they be selected for the vertical sampling.

Additionally, if there are shallow and deep piezometers that are part of base wide remediation efforts, these could be used to evaluate potentiometric differences. Further, the difference between the first encountered water level and the equilibrated water levels may indicate a confining condition and that there may be an upward gradient.

The potential for vapor impact in the vicinity of the housing units was not presented. A screening evaluation of potential vapor impacts will be evaluated as part of the follow-on risk management report. If the potential for vapor impacts exists, then additional soil vapor sampling may be needed.

Identification of Receptors

Because of the present land use at TAFB, and the presumed large distances to potential human and ecological risk receptors downgradient, risks to human health through common exposure pathways and to the environment appear to be low. However, we have not been able to identify locations and screened intervals of existing water supply wells downgradient of the TAFB site in the site documentation. Such information needs to be provided if available to apply risk based corrective action to the site.

Summary

Subsurface investigations conducted at TAFB appear to be satisfactory in terms of characterizing the nature of the subsurface environment and the distribution of contaminants. The natural attenuation evidence presented in the TS has provided credible evidence that dissolved FHCs in groundwater underlying the site are indeed undergoing bioattenuation to some extent. To prepare the Expert Committee's site risk management report, the following additional data is requested.

- (1) Additional time series sampling of NSGS monitor wells for BTEX and MTBE.
- (2) Information that validates the assumptions of no vertical migration into the Norton Shale unit. This may be provided by vertical sampling for BTEX and MTBE at MW-135 and MW-138 within the NSGS plume or by piezometric data.
- (3) Downgradient water supply well locations and screened intervals (if available).
- (4) Clarification of the completion of the NSGS excavations and the role of onsite precipitation recharge.

We look forward to preparing the TAFB site risk management report following receipt of this information.

Sincerely,



David W. Rice
Project Director and
Expert Committee Lead for Travis AFB.

Appendix B

Uncertainty Analyses of Fuel Hydrocarbon Bioattenuation Signatures in Groundwater by Probabilistic Modeling

Acknowledgments

This study is part of the U.S. Department of Defense Petroleum Hydrocarbon Demonstration Program (PHCDP). Funding for this work has been provided by the U.S. Air Force Center for Environmental Excellence (AFCEE), Environmental Restoration Directorate, Technology Transfer Division (ERT) at Brooks Air Force Base, Texas. The authors wish to thank Marty Faile, Patrick Haas, and Charles Lee (AFCEE) and Dave Rice and Richard Ragaini (Lawrence Livermore National Laboratory) for their guidance and support.

Appendix B

Uncertainty Analyses of Fuel Hydrocarbon Bioattenuation Signatures in Groundwater by Probabilistic Modeling

Abstract

Natural attenuation processes, primarily bioattenuation, are now in many instances viewed as the preferred means for remediating groundwater contaminated by fuel hydrocarbons from leaking underground fuel tanks (LUFTs). An understanding of the uncertainties associated with natural attenuation processes, and their capacity to limit plume migration, is therefore of great importance. In this study, a probabilistic modeling approach is developed to quantify uncertainties involved in the impact of bioattenuation on hydrocarbon plume behavior. The approach is based on Monte Carlo analyses of an analytical solution to the advective-dispersive solute transport equation, including a first-order degradation term, coupled with mass balance constraints on electron acceptor utilization. Empirical probability distributions for governing parameters are provided as input to the model; the resulting probability distributions of forecast concentrations (hydrocarbon components and geochemical indicator species) provide insights into the uncertainty associated with concentration values at well locations. Sensitivity analyses indicate which uncertainties in the governing parameters have the greatest impact on the variability in concentration forecasts. Application of the model to an existing LUFT site illustrates the degree of uncertainty associated with hydrocarbon concentrations and geochemical indicators at individual site monitoring wells as well as the roles of various parameter assumptions (e.g., hydraulic conductivity, first-order decay coefficient, source term) in influencing forecast variability. Such information is useful for risk management planning in that the degree of confidence that bioattenuation will limit the impact of a hydrocarbon plume on potential risk receptors may be quantified.

Introduction

Fuel hydrocarbon compounds (FHCs) associated with leaking underground tanks and pipelines are common shallow groundwater contaminants. Aromatic constituents such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are of the greatest regulatory concern due to their relatively high solubility in water and possible long-term health effects (most notably pertaining to benzene). However, it has become widely recognized that BTEX compounds will biodegrade under a variety of conditions. Moreover, the recent study by Rice et al. (1995) showed that lengths of BTEX plumes in shallow groundwater in California tend to be limited to distances less than 260 feet, a finding confirmed by Buscheck et al. (1996). Natural attenuation mechanisms (i.e., primarily biodegradation, but also possibly including dispersion, retardation, and other processes) were cited as the probable explanation.

Regulators, site stakeholders, and the scientific community have begun to recognize that natural attenuation processes can often be called upon to effectively remediate groundwater contaminated with FHCs. To protect public health and the environment, the decision to proceed with natural attenuation as a sole means for cleanup of impacted groundwater at a given site must address the uncertainties associated with this course of action. These uncertainties can be divided into two primary issues: (1) whether or not biodegradation reactions are indeed actively destroying hydrocarbon contaminants at a given site, and (2) whether or not natural attenuation will prevent the further downgradient migration of a dissolved plume which would otherwise threaten potential risk receptors.

To address these issues, a probabilistic modeling approach has been developed to provide a means for quantifying these types of uncertainties. This approach involves the application of a Monte Carlo simulation technique to an analytical solution of the advective-dispersive transport equation, which includes a degradation term, under the influence of a constant concentration line source. The Monte Carlo approach allows uncertainties in hydrogeologic data (e.g., hydraulic conductivity, hydraulic gradient magnitude and direction) and chemical data (e.g., background electron acceptor concentrations, degradation rates) to be translated into uncertainties regarding contaminant and electron acceptor concentrations at individual wells or variations in plume length with time. In addition, sensitivity analyses comparing uncertainties in input parameters to uncertainties in forecast results can provide insights into which types of data are most critical for quantifying the behavior of plumes undergoing natural attenuation.

The model proposed in this study has been applied to groundwater quality data collected from the North-South Gas Station (NSGS) site at Travis Air Force Base (Travis AFB) in Fairfield, California (Figure B-1). Forecast results from this study are generally consistent with observed site data in terms of probability distributions of BTEX and geochemical indicator concentrations. Moreover, forecast probability distributions of BTEX plume lengths suggest that the plume is likely to remain in a steady-state condition (if not decline) over time. Sensitivity analyses suggest that uncertainty in mean hydraulic conductivity is the most important factor in contributing to variance in forecast BTEX concentrations, particularly far downgradient of the source area, with uncertainty in the decay coefficient playing a lesser, although significant, role. With regard to geochemical indicator parameters, both uncertainty in background concentrations as well as in mean hydraulic conductivity contribute to variances in forecast geochemical indicator species concentrations.

Methods

Modeling Approach

Although analytical solutions to the advective-dispersive solute transport equation lack the general flexibility offered by numerical methods, they do serve as effective probability distribution models for contaminant concentrations as a function of space and time in many situations. In particular, in the case of many leaking underground fuel tank sites, sufficient spatial resolution of subsurface stratigraphy is lacking to the point where numerical simulation is not justified. In many cases, analytical solutions will serve equally well as screening models. Furthermore, because of their simplicity, analytical solutions are ideal for Monte Carlo analyses.

Domenico (1987) presented a closed-form analytical solution for one-, two-, or three-dimensional advective-dispersive transport of a solute away from a continuous line or vertical plane source in an idealized homogeneous medium under uniform flow conditions. The two-dimensional form of this solution is,

$$C(x, y, t) = \left(\frac{C_0}{4} \right) \exp \left\{ \left(\frac{x}{2\alpha_x} \right) \left[1 - \left(1 + \frac{4R\lambda\alpha_x}{v} \right)^{1/2} \right] \right\} \quad (1)$$

$$\bullet \operatorname{erfc} \left[\frac{x - \frac{v}{R} t (1 + 4R\lambda\alpha_x / v)^{1/2}}{2 \left(\alpha_x \frac{v}{R} t \right)^{1/2}} \right] \bullet \left\{ \operatorname{erf} \left[\frac{(y + Y/2)}{2(\alpha_y x)^{1/2}} \right] - \operatorname{erf} \left[\frac{(y - Y/2)}{2(\alpha_y x)^{1/2}} \right] \right\}$$

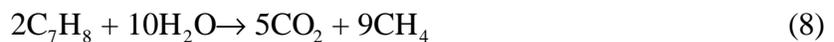
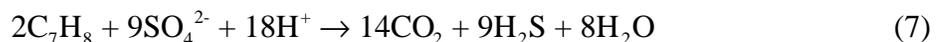
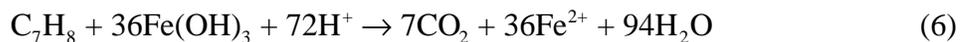
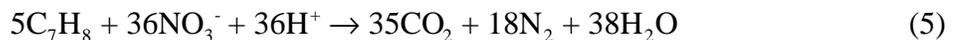
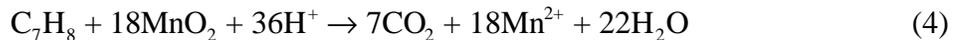
where C_0 refers to the source concentration (constant with time), α_x the longitudinal dispersivity, α_y the transverse dispersivity, λ the first-order decay coefficient, v the groundwater pore velocity,

R the retardation coefficient, Y the width of the line source, t the monitor time, and x and y the Cartesian coordinates of the monitor point relative to the source.

In this study, model development consisted of programming Eq. (1) into a Microsoft Excel spreadsheet and then using the Crystal Ball add-in package (Decisioneering, Inc., 1996) for Excel to construct Monte Carlo simulations of solute concentration utilizing prescribed probability distributions for the governing parameters. While Eq. (1) may be used to directly simulate spatial and temporal variations in BTEX concentrations, indirect stoichiometric calculations must be used to estimate changes in geochemical indicator parameters. At any monitoring location (x , y), the cumulative quantity of BTEX which has undergone biodegradation, ΔC , integrated over time and space, is given by,

$$\Delta C = C_{\text{conservative}} - C_{\text{decay}} \quad (2)$$

Thus, the amount of BTEX mineralized to carbon dioxide may be estimated from the difference between predicted BTEX concentrations using a conservative (i.e., non-bioattenuating model) and concentrations predicted with a finite decay coefficient. The oxidation of such a quantity of BTEX requires the reduction of an electron acceptor(s) as described by simple reaction stoichiometry (assuming toluene as a surrogate for BTEX),



These reactions are listed in order of thermodynamic favorability; microorganisms obtain the greatest energy benefit by using oxygen as an electron acceptor; while the reduction of carbon dioxide to methane provides the least amount of energy. To address this sequence in the model, the quantity of BTEX biodegraded at a given point is first calculated by Eqs. (1) and (2). Then, electron acceptor concentrations are adjusted, in sequence, based on stoichiometry until all of the mineralized BTEX is accounted for. Thus, the spatial distributions of electron acceptors are effectively calculated by a superposition model. The model ignores the conversion of a fraction of the hydrocarbon material into cell biomass. If suitable stoichiometric reactions are available describing this process, they may be incorporated into the model scheme as well.

In most near-neutral pH waters, an analysis of total alkalinity usually represents bicarbonate alkalinity, the dominant species of inorganic carbon under such conditions. Assuming that most of the CO_2 produced in the BTEX mineralization reactions is converted to bicarbonate, local changes in total alkalinity in response to bioattenuation can be estimated by the model in a semi-quantitative sense. Methane concentrations can also be predicted by the model. However, because the simple first-order decay coefficient used in Eq. (1) does not account for any limitations in biodegradation rates as conditions become methanogenic, predicted mineralization of very large quantities of BTEX will simply lead to the production of large quantities of methane (well above solubility limits). Thus, methane concentrations predicted by this model cannot be viewed in a strictly quantitative sense but rather should serve simply as an indicator of probable methanogenic conditions.

It should be noted that in cases where significant retardation of BTEX migration occurs because of adsorption, the calculated spatial distributions of geochemical indicators based upon the superposition model must be interpreted with caution. This is because the superposition model

assumes that all constituents are characterized by the same mobility; a constraint imposed by superposition of the analytical solution. Thus, realizations which use a retardation coefficient greater than 1.0 for BTEX migration assume the same degree of retardation for all electron acceptors, methane, and alkalinity.

Example Site Parameter Estimation

The Crystal Ball Excel add-in package performs Monte Carlo simulations by utilizing user-specified *assumptions* (parameters and their probability distribution functions, representing uncertainty in data) to produce *forecasts* (the output of a functional relationship, such as Eq. (1), which itself becomes a probability distribution function). In this study, each Monte Carlo simulation consisted of running 20,000 realizations in the prescribed parameter space at each monitoring well location. Frequency distributions for the forecasts values (i.e., concentration probability forecasts) were tallied along with parameter sensitivity analyses. The forecast probabilities were then compared to measured concentrations of each constituent. For the NSGS site model, the assumptions and their distributions (and the basis for the distributions) are listed on Table B-1. It must be recognized that these probability distributions, for the most part, reflect empirical observations and do not necessarily represent true distribution models for the parameters under consideration. For example, mean hydraulic conductivity probability distributions reflect only estimated hydraulic conductivities from a small number of pumping tests and slug tests performed on site wells. As such, only a limited portion of the true distribution of sediment types present in the subsurface is represented, so forecast results must always be treated with the appropriate degree of caution.

Forecasts produced by the model include total BTEX, oxygen, manganese, nitrate, iron, sulfate, methane, and alkalinity at a various well locations after a given amount of elapsed time since the initiation of the (assumed) continuous source. For simplicity, total BTEX concentration was used to represent the soluble, biodegradable portion of the hydrocarbon product, with toluene serving as a surrogate for BTEX in calculating reaction stoichiometry. Representative values for aqueous solubility and K_{oc} for total BTEX were chosen using weighted averages based upon the mean composition of 87 octane unleaded gasoline (Kaplan and Galperin, 1996). Electron acceptor, methane, and alkalinity concentrations were estimated based upon Eqs. (1) and (2), reaction stoichiometry (Eqs. 3-8), and assumptions concerning background site data (i.e., probability distributions fit to site monitoring wells where total BTEX was not found above detection limits). In the cases of manganese and iron, the electron acceptor occurs in the form of mineral-phase oxides, so an aqueous background concentration cannot be specified directly in the same manner as dissolved oxygen, nitrate, or sulfate. Instead, probability distributions were fit to dissolved manganese and iron concentrations measured in wells in which total BTEX was detected (reduced forms of the two metals), and this distribution was assumed to reflect the capacity of these electron acceptors to oxidize BTEX in background conditions. Of course, this assumption does not take into account mineral precipitation side reactions, such as precipitation of iron sulfide, magnetite, or manganese carbonate, which could also impact dissolved concentrations of these metals.

Prior to running each realization of the Monte Carlo analysis, certain assumptions must be integrated into parameters which are used directly as input in the Domenico (1987) model. For example, flow velocity was not measured directly at the site and hence a probability distribution is not available. However, Darcy's law may be used to calculate velocity directly from assumptions which have prescribed probability distributions (i.e., mean hydraulic conductivity, K , hydraulic gradient, ∇h , and porosity, ϕ),

$$v = -\frac{K\nabla h}{\phi} \quad (9)$$

Retardation due to dissolved hydrocarbon (BTEX) partitioning onto organic carbon in site sediments is modeled by calculating a retardation coefficient for each Monte Carlo realization by the relationship,

$$R = 1 + \frac{K_{oc} f_{oc} \rho_b}{\phi} \quad (10)$$

using a weighted mean organic carbon partitioning coefficient, K_{oc} , for BTEX (282 ml/g) and prescribed probability distributions for the other parameters (f_{oc} , organic carbon fraction of the sediment, and ρ_b , the soil bulk density) on the right-hand-side of Eq. (10).

Analysis

Evidence Supporting Bioattenuation

Forecast BTEX Concentration Distributions

Forecast probabilities and actual measurements of total BTEX (August/September, 1995 sampling event) at four distinct well locations are shown on Figure B-2. Each well represents a different region of the subsurface in relation to the spill: immediately downgradient of the source area (MW-138), distal portion of the BTEX plume (MW-210), immediately downgradient of the leading edge of the plume (MW-214), and far downgradient of the plume (MP-7). The forecast probability distributions are consistent with expectation, with higher total BTEX concentrations predicted as likely closer to the source (MW-138) and highly unlikely far downgradient (MP-7). In general, the forecast probability distributions are also consistent with field measurements, with measured concentrations falling into the largest probability frequency group for three out of the four wells (forecast concentration probability for total BTEX in MW-210 underestimated the observed concentration of 4.1 mg/L).

The cumulative distribution of measured total BTEX in 12 of the wells which exhibited detectable BTEX concentrations during the August/September, 1995 sampling event is shown on Figure B-3. Cumulative distributions of forecast BTEX concentrations for the same set of wells are also shown on Figure B-3. In this case, three different cumulative distributions were created by separately tallying the 50th-, 55th-, and 60th-percentile forecast values for all 12 wells. As indicated on the plot, the forecast 55th-percentile level not only closely matches the median observed value but also reproduces the observed variance fairly well. Further analysis shows that the median percentile value on which each measured data point fell onto its respective forecast cumulative distribution function was 58%, with an average value of 57% and a standard deviation of 15%. These results indicate that, taken as a whole, the model produced good forecasts of the observed distribution of total BTEX concentrations, producing only minor systematic underestimates.

To gain insight into how the forecast and measured BTEX concentrations correlate spatially, a set of 12 wells with detectable BTEX concentrations were plotted with well symbols drawn according to where the measured BTEX concentration fell on its respective forecast cumulative distribution (Figure B-4). For simplicity, the wells were divided into three groups: those with measured values falling below the 40th-percentile (i.e., wells where the model tended to overestimate BTEX concentrations), those between the 40th- and 60th-percentiles (i.e., wells where measured concentrations were close to the central tendency of the model forecasts), and those greater than the 60th-percentile (i.e., wells where the model tended to underestimate BTEX concentrations). This analysis suggests that the model tends to slightly overestimate BTEX concentrations perpendicular to the centerline of plume movement (toward the southeast), while concentrations along the centerline tend to be underestimated by the model. One possible explanation for this observation is that a subsurface feature such as a buried stream channel may be controlling transport of the plume, suppressing the lateral spreading predicted by the standard dispersion model and concentrating more of the dissolved components along the centerline.

Forecast Geochemical Indicator Concentration Distributions

Forecast probability distributions and measured concentrations (August/September, 1995 sampling event) of dissolved oxygen, nitrate, sulfate, iron, manganese, alkalinity, and methane are

shown on Figures 5 through 11, respectively for MW-138, MW-210, MW-214, and MP-7. For each geochemical indicator, forecast probability distributions are generally consistent with both expectation and observation. In the case of dissolved oxygen (Figure B-5), a slight increase in probable concentration values is forecast further downgradient of the source, although concentrations are forecast to remain low in general. The observed progressive increase in dissolved oxygen matches the forecast patterns. Forecast probability distributions for nitrate (Figure B-6) are analogous to those of dissolved oxygen, although the change with distance downgradient is slightly more pronounced. In this case, the model tended to underestimate measured nitrate concentrations in the two wells furthest downgradient (MW-214 and MP-7).

Forecast probability distributions of sulfate (Figure B-7) show a far more pronounced variability with distance from the source than those of oxygen and nitrate. This is a result of the relatively high concentration of sulfate which allows it to exist in surplus quantities as an electron acceptor in many of the Monte Carlo realizations. Consequently, sulfate concentrations are predicted to be relatively low in the immediate vicinity of the source but increase significantly in the downgradient direction. Forecast probability distributions are consistent with observed sulfate concentrations in the four monitoring wells, with significantly depleted sulfate predicted as well as measured in MW-138 and with significantly higher concentrations in the downgradient direction.

Forecast probability distributions of iron and manganese (Figures B-8 and B-9, respectively) are similar to one another, with the highest concentrations forecast nearest the source and the likelihood of very low concentrations increasing rapidly in the downgradient direction. In general, the forecast values for both metals appear consistent with measured concentrations.

Forecast probability distributions of alkalinity (Figure B-10) show a shift from generally high values near the source toward lower values further downgradient, reflecting the diminishing influence of hydrocarbon mineralization on inorganic carbon away from the highest hydrocarbon concentrations. Forecast probability distributions match the observed values fairly well, with measured values corresponding to the largest probability frequency group for three of the four wells (the concentration in MW-210, 602 mg/L, falls into the second largest probability distribution group for that well).

As noted earlier, forecast methane concentrations, and hence forecast probability distributions, are in reality only qualitative indicators of methanogenic conditions because solubility limitations on methane are not accounted for by the model. Thus, the forecast probability distributions of methane (Figure B-11) simply reflect whether or not methanogenic conditions are likely (defined here for simplicity as 1 mg/L concentration of methane or higher). Forecast probability distributions of methanogenic activity are qualitatively consistent with observation, although the methanogenic activity noted in MW-138 was not predicted as likely by the model (i.e., probability less than a 30%).

Sensitivity of Forecasts to Parameter Assumptions

Sensitivity analyses provide insight into which probability distribution assumptions for the governing parameters have the greatest impact on variability in forecast probability distributions. The Crystal Ball add-in package to Microsoft Excel performs sensitivity analyses of forecast values on user-prescribed assumptions. This is accomplished using rank-based correlation; contributions to variance are calculated on a percentage basis by squaring rank correlation coefficients and normalizing the results.

Sensitivity analyses of forecast BTEX concentrations to the prescribed parameter assumptions are shown on Table B-2. As expected, BTEX concentrations are negatively correlated (by rank) with the decay coefficient, while positive correlations are observed for hydraulic conductivity, gradient, and, to a minor extent, the α_x -to-plume length ratio. By comparison, the uncertainty in the remaining assumptions (source location, gradient direction, monitor time, transverse dispersivity, soil TOC, elapsed time, background geochemical composition) did not significantly impact forecast results. This analysis indicates that uncertainty in groundwater velocity (reflecting variations in hydraulic conductivity and gradient) is the most significant factor influencing forecast BTEX concentrations, with the decay coefficient also having a significant effect, particularly in the vicinity of the source.

Sensitivity analyses of forecast geochemical indicator species concentrations to the prescribed assumptions are shown on Table B-3. Forecast concentrations of geochemical indicators differ somewhat in parameter sensitivity from that of BTEX. Near the source area, uncertainty in background concentrations of the indicator parameters (manganese, iron, sulfate, methane, alkalinity) appear have the greatest influence on their respective forecast concentration probability distributions. Groundwater velocity and the decay coefficient in turn show little impact. In the cases of manganese and iron, sensitivity to background uncertainty results from the low attenuation capacity offered by these electron acceptors in Travis AFB groundwater. In the immediate vicinity of the source area, even a limited degree of BTEX degradation utilizes all of the available manganese and iron. Hence, the amount utilized correlates directly with the amount available. In the case of sulfate, the same sensitivity is observed, but for the opposite reason: background sulfate concentrations are high enough that BTEX degradation exerts only a partial influence in comparison to background variability. Whenever sulfate is completely utilized, methanogenesis immediately commences in the simple stoichiometric model, explaining the influence of the uncertainty in background sulfate concentrations on the forecast concentrations of methane. By analogy to sulfate, forecast alkalinity is most sensitive to the background alkalinity because the uncertainty in the natural background exceeds the variability imparted by BTEX degradation.

Further downgradient of the source area, geochemical indicator sensitivity relationships differ from those characteristic of the source area. Variability in forecast concentrations of dissolved oxygen, manganese, nitrate, and iron tend to correlate most strongly with uncertainty in hydraulic conductivity and gradient, indicating a high degree of sensitivity to the groundwater flow velocity. This is because each of these electron acceptors is likely to be entirely utilized in the source area, thus changes in concentration in the downgradient direction are largely a reflection of the migration rate of the anaerobic shadow left by the BTEX plume. Forecast concentrations of sulfate and alkalinity far downgradient continue to show the same sensitivity to background concentrations as noted near the source area.

Forecast Future Behavior: Plume Length as a Function of Time

Ultimately, the added value in using a probabilistic approach to model reactive transport of BTEX lies in forecasting future risk associated with persistence of the contamination problem. One measure of risk associated with BTEX groundwater contamination is plume length; longer plume lengths obviously pose more of a threat to any existing or potential downgradient risk receptors (e.g., water-supply wells, ecological receptors) than do shorter plumes.

A conservative approach for forecasting probable plume lengths is to assume a continuous source of contaminants to groundwater with time (e.g., a lens of floating free product which is never depleted of soluble BTEX components). Under such conditions, a plume undergoing degradation can be expected to stabilize into a steady-state configuration when the rate of contaminant influx from the source is balanced by contaminant loss through degradation, integrated across the extent of the plume. This steady-state plume can be evaluated by using the Domenico (1987) solution to predict concentrations downgradient of the source (centerline), then employing a suitable search algorithm (e.g., bisection, Newton's method) to find the downgradient location at which a certain concentration is reached. Plume length may then be defined as the distance from the source to such a location.

This approach was used to generate forecast probability distributions of total BTEX plume lengths, using the hydrogeological assumptions given on Table B-1, for 1995 and 30 years into the future, 2025. For comparison, a third set of plume lengths forecasts was generated for the year 2025, but without a biodegradation term. A single source term was used to simplify the analysis. The results of the plume length forecasting are shown on Figure B-12 (assuming a plume length defined by the 10 parts-per-billion contour, as suggested by Rice et al., 1995). Although the variability in forecast plume lengths is large, the probability distributions between 1995 and 2025 appear to be very similar, suggesting that pronounced plume movement during that time is probably not likely, given the assumptions used. In contrast, the no-degradation scenario for the year 2025 shows a very distinct shift in the plume length probability distribution toward longer lengths, illustrating the role of bioattenuation in limiting downgradient plume migration.

Discussion and Summary

The various risks associated with most cases of groundwater contamination generally involve the migration of contaminants to downgradient water supply wells (i.e., human health risks), streams and wetlands (i.e., ecological risks), or adjacent properties (i.e., financial risks for the stakeholders). In the case of FHCs, natural attenuation is now being frequently called upon as the primary means of groundwater remediation for many sites. Therefore, in the context of risk management, the most important issue to be addressed is whether or not natural attenuation offers a sufficiently high probability that the plume will be fully restrained from further migration.

Evidence supporting the role of bioattenuation in limiting FHC plumes may be either primary or secondary in nature. Primary lines of evidence include quantitative demonstration of plume stability or plume shrinkage based upon trends in historical groundwater quality data. Secondary evidence includes spatial variations in geochemical indicator parameters of bioattenuation (dissolved oxygen, nitrate, sulfate, iron, manganese, methane, alkalinity). Primary evidence generally provides the strongest indication as to the role of natural attenuation at any given site. However, such evidence is commonly not available because adequate historical monitoring may not exist. As a consequence, means for assessing the secondary lines of evidence must be developed and explored.

Probabilistic modeling can serve as a powerful tool for addressing the uncertainty associated with the role of natural attenuation at FHC sites. A procedure for conducting this type of modeling consists of integrated Monte Carlo analysis using analytical solutions to the advective-dispersive equation coupled with mass balance constraints on the utilization of electron acceptor species. The specific steps involved in the procedure include:

- (1) Review pertinent site hydrogeological and geochemical data to develop empirical probability distribution functions for the parameters of interest. Such parameters will include hydraulic conductivity, hydraulic gradient, nature of the source (concentration, spatial extent, time of original release), first-order degradation rate constant, soil organic carbon content, background electron acceptor concentrations, and so forth. When such data are not readily available, broad distributions of values from the general literature may be substituted, but it is expected that this will often result in greater uncertainty in probability forecasts. It is important to note that the parameters (and their distributions) used as input for the model are not derived by model calibration to the observed data. To prevent bias, each must be estimated independently.
- (2) Conduct multiple Monte Carlo realizations to quantify probability distributions of contaminant (BTEX) and geochemical indicator species concentrations at monitoring well locations. Compare observed site data with forecast probability distributions.
- (3) Perform sensitivity studies on the impact of uncertainties in parameter assumptions on variability in forecast distributions. Such analyses may provide insights into which parameter uncertainties must be refined to improve forecasts.
- (4) Perform plume length analysis to forecast future plume behavior.

This approach has been applied to the analysis of a BTEX plume associated with the NSGS site at Travis AFB. Simulations have yielded probability distribution functions (distributions of total BTEX, geochemical indicator parameters) which are generally consistent with observations at the site. Sensitivity analyses indicate that variations in groundwater velocity (calculated from probability distributions of hydraulic conductivity, gradient, and porosity) exert the greatest impact on variances in BTEX concentrations, with the decay coefficient also having a significant effect, particularly close to the source. Variances in geochemical indicator parameters are affected primarily by their background concentration probability distribution functions, although groundwater velocity has the largest affect on dissolved oxygen, nitrate, iron, and manganese far downgradient of the source. Plume length forecasts show a considerable amount of uncertainty with regard to probable length of the total BTEX plume. Nevertheless, there is very little difference between the forecast plume length probability distributions for 1995 and 2025, suggesting little potential for substantial further plume migration.

Probabilistic modeling analysis can provide insights into the likelihood that bioattenuation is limiting plume migration. However, the definition of what constitutes a sufficiently high likelihood or probability for site closure is beyond the scope of this approach. Rather, such questions are entirely context-dependent upon nearby risk receptors and probable beneficial uses of the groundwater and thus are better suited to discussions of regulatory policy.

Acknowledgments

This study is part of the U.S. Department of Defense Petroleum Hydrocarbon Demonstration Program (PHCDP). Funding for this work has been provided by the U.S. Air Force Center for Environmental Excellence (AFCEE), Environmental Restoration Directorate, Technology Transfer Division (ERT) at Brooks Air Force Base, Texas. The authors wish to thank Marty Faile, Patrick Haas, and Charles Lee (AFCEE) and Dave Rice and Richard Ragaini (Lawrence Livermore National Laboratory) for their guidance and support.

References

- Busheck, T. E., D. C. Wickland, and D. L. Kuehne. 1996. Multiple lines of evidence to demonstrate natural attenuation of petroleum hydrocarbons. 1996. Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, Houston, TX, November 13-15, 1996. National Groundwater Association/API.
- Decisioneering, Inc. 1996. Crystal ball: forecasting and risk analysis for spreadsheet users. Decisioneering, Inc., Aurora, CO.
- Domenico, P. A. 1987. An analytical model for multidimensional transport of a decaying contaminant species. *Journal of Hydrology*, v. 91, pp. 49-58.
- Kaplan, I. R. and Y. Galperin. 1996. How to recognize a hydrocarbon fuel in the environment and estimate its age of release. *Groundwater and Soil Contamination: Technical Preparation and Litigation Management*. T. J. Bois, and B. J. Luther, eds. John Wiley and Sons, 1996.
- Parsons Engineering Science. 1996. Final treatability study to evaluate intrinsic remediation at the north and south gas stations, Travis Air Force Base, CA. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.
- Rice, D. W., R. D. Grose, J. C. Michaelson, B. P. Dooher, D. H. MacQueen, S. J. Cullen, W. E. Kastenberg, L. E. Everett, and M. A. Marino. 1995. California leaking underground fuel tank (LUFT) historical case analyses. Lawrence Livermore National Laboratory, Livermore, CA. (UCRL-AR-122207).

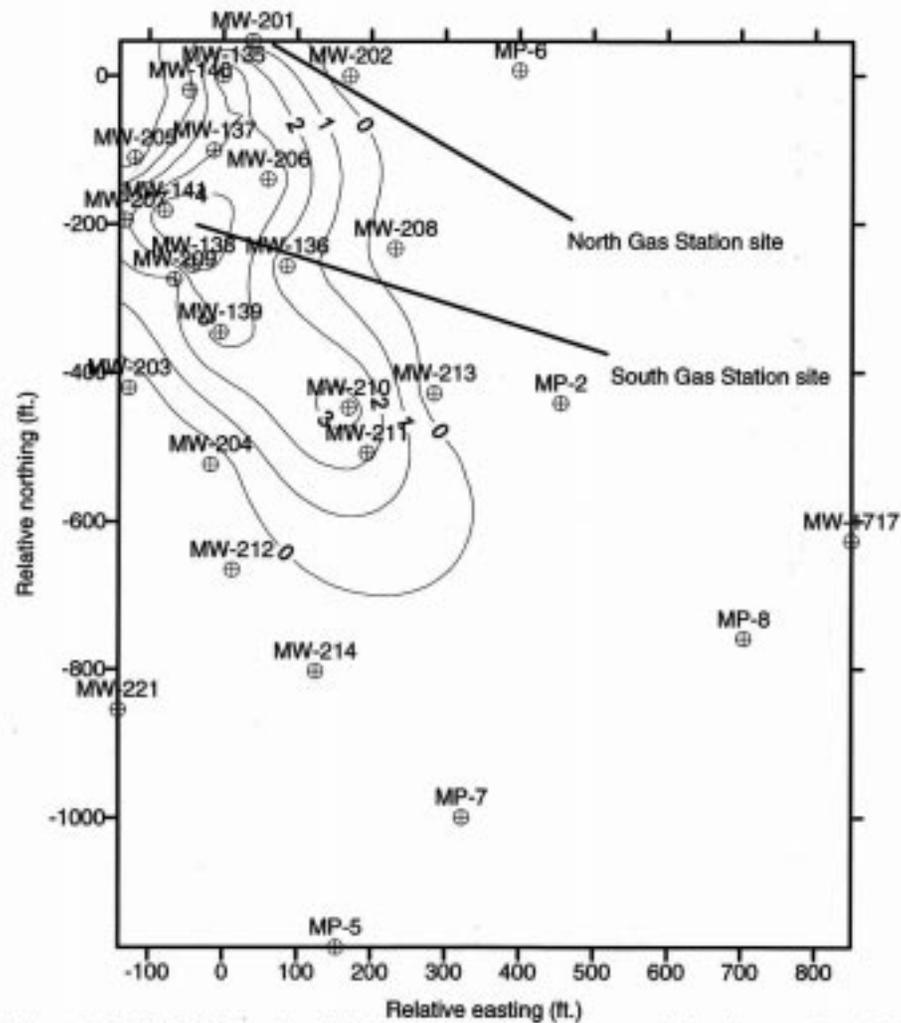


Figure B-1. NSGS site at Travis AFB, showing source areas, well locations, and total BTEX concentrations (log parts-per-billion).

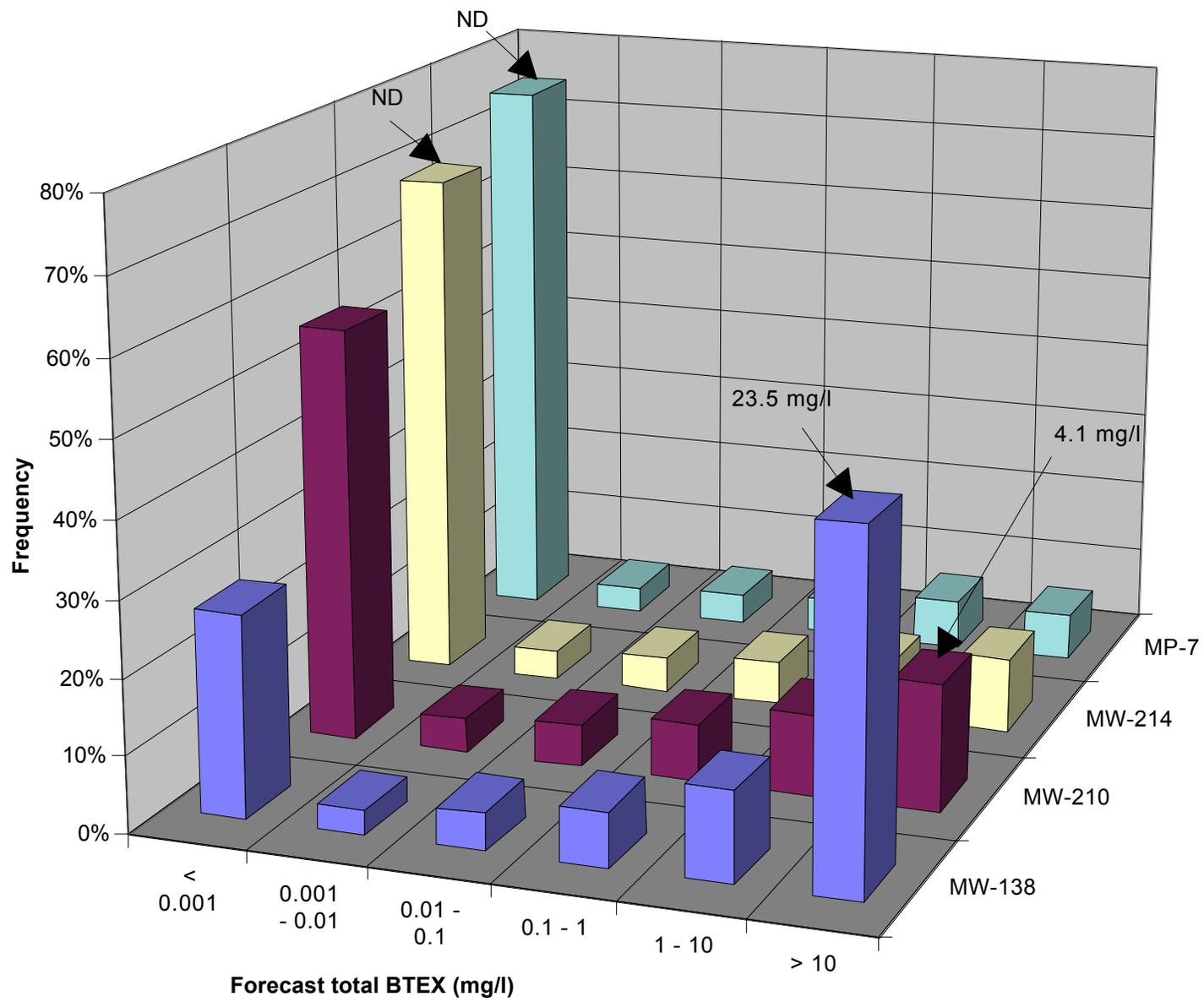


Figure B-2. Frequency distributions of total BTEX concentrations in selected monitoring wells.

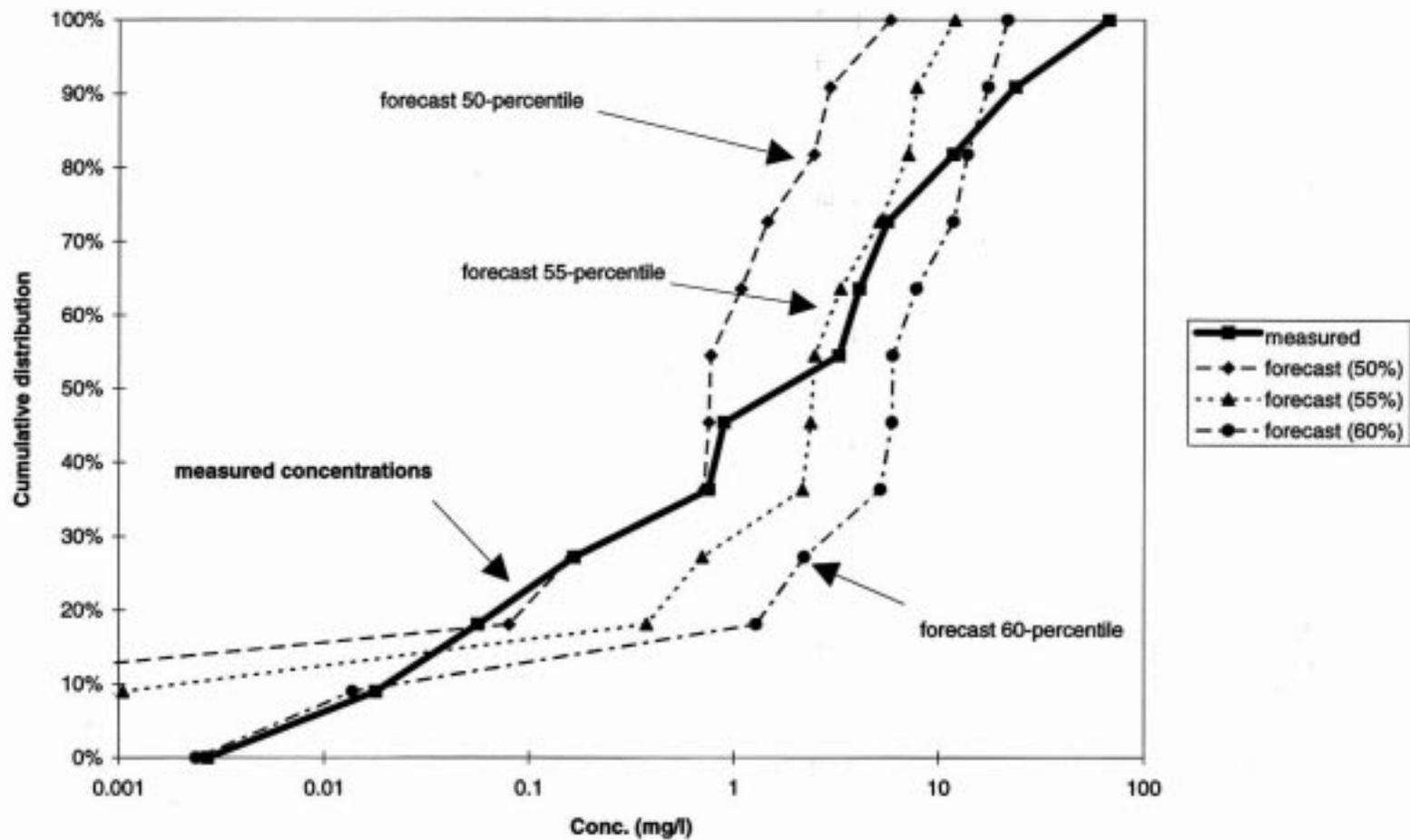


Figure B-3. Cumulative distributions of forecast total BTEX concentrations (50th-, 55th-, and 60th-percentiles) and measured BTEX concentrations at 12 wells with detectable dissolved hydrocarbons.

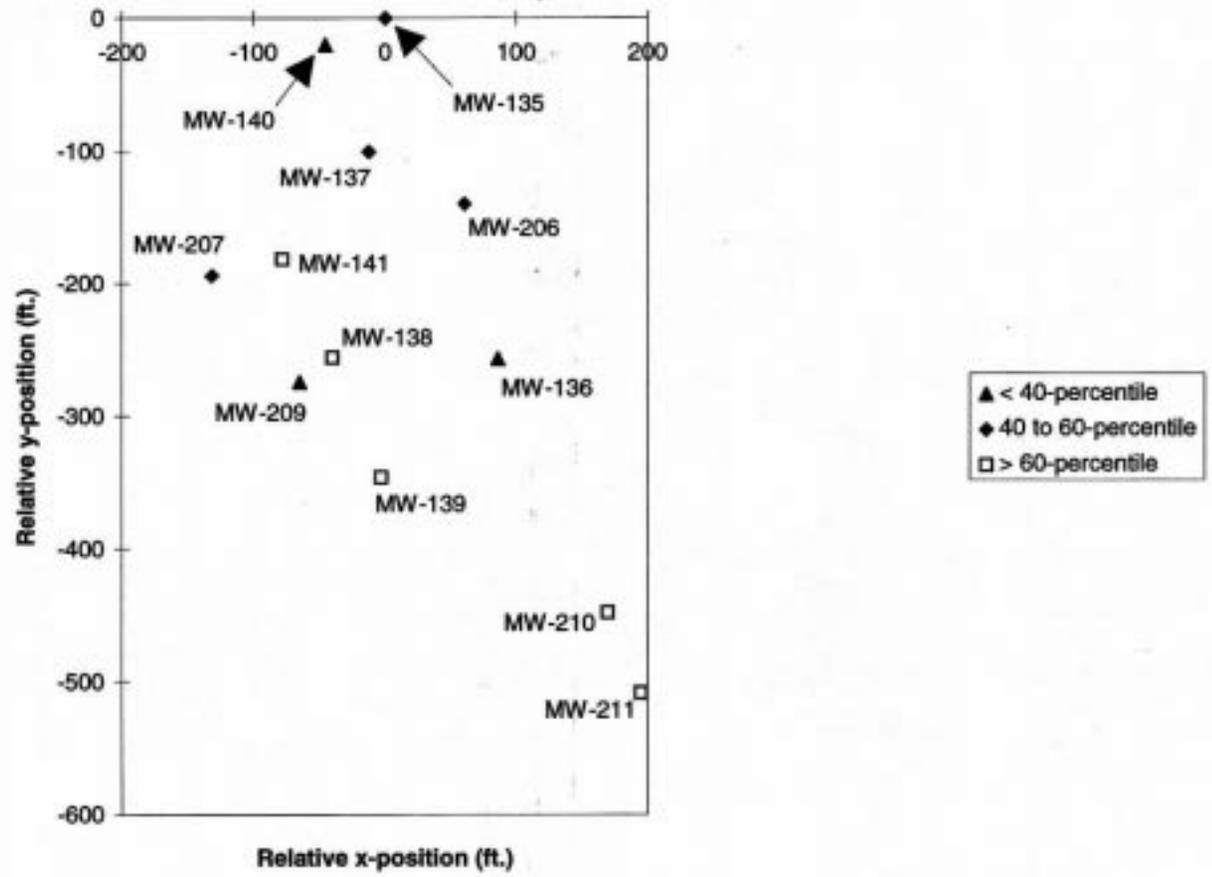


Figure B-4. Spatial variability in forecast total BTEX concentrations as compared to measured concentrations.

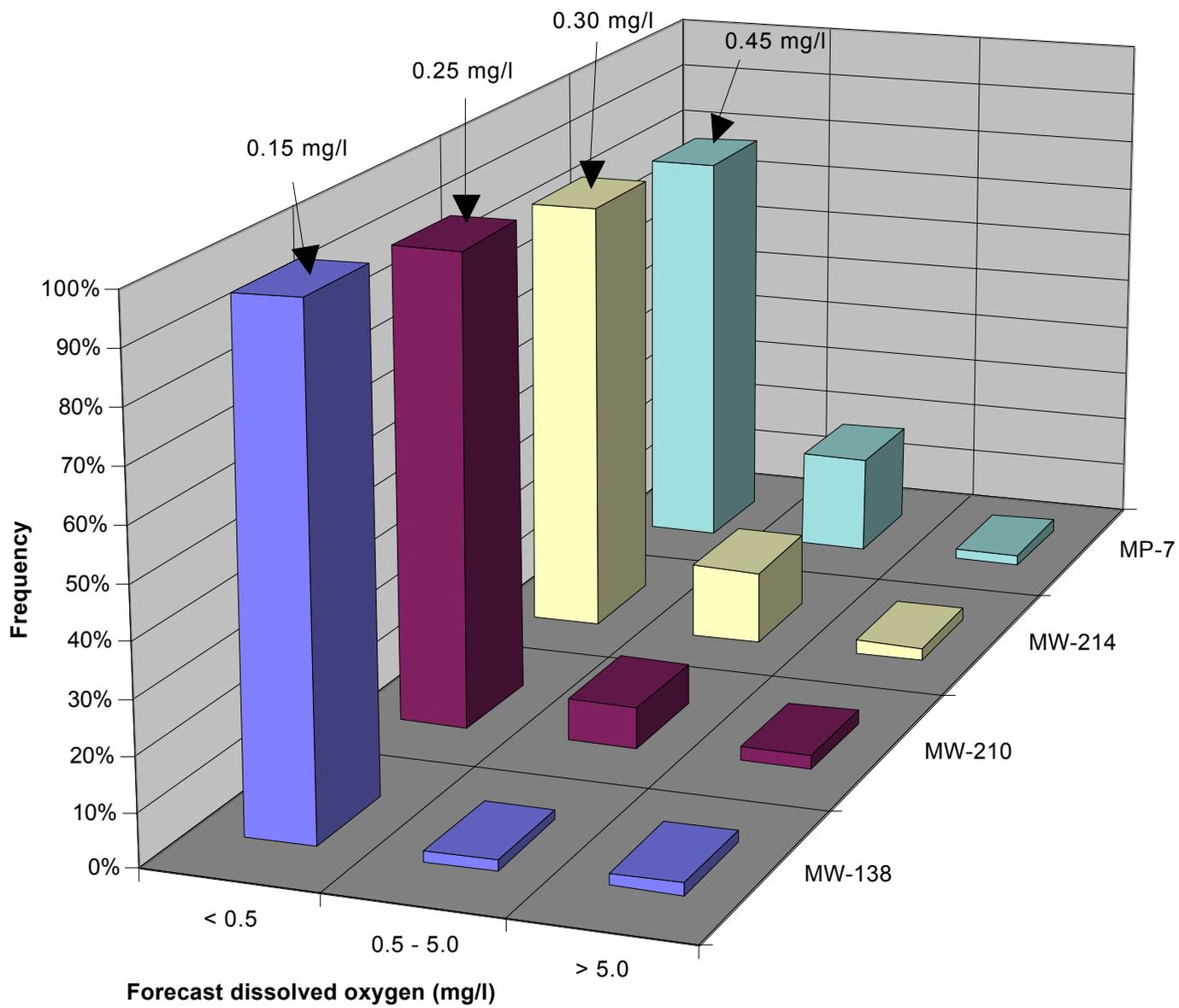


Figure B-5. Frequency distributions of forecast dissolved oxygen concentrations in selected monitoring wells.

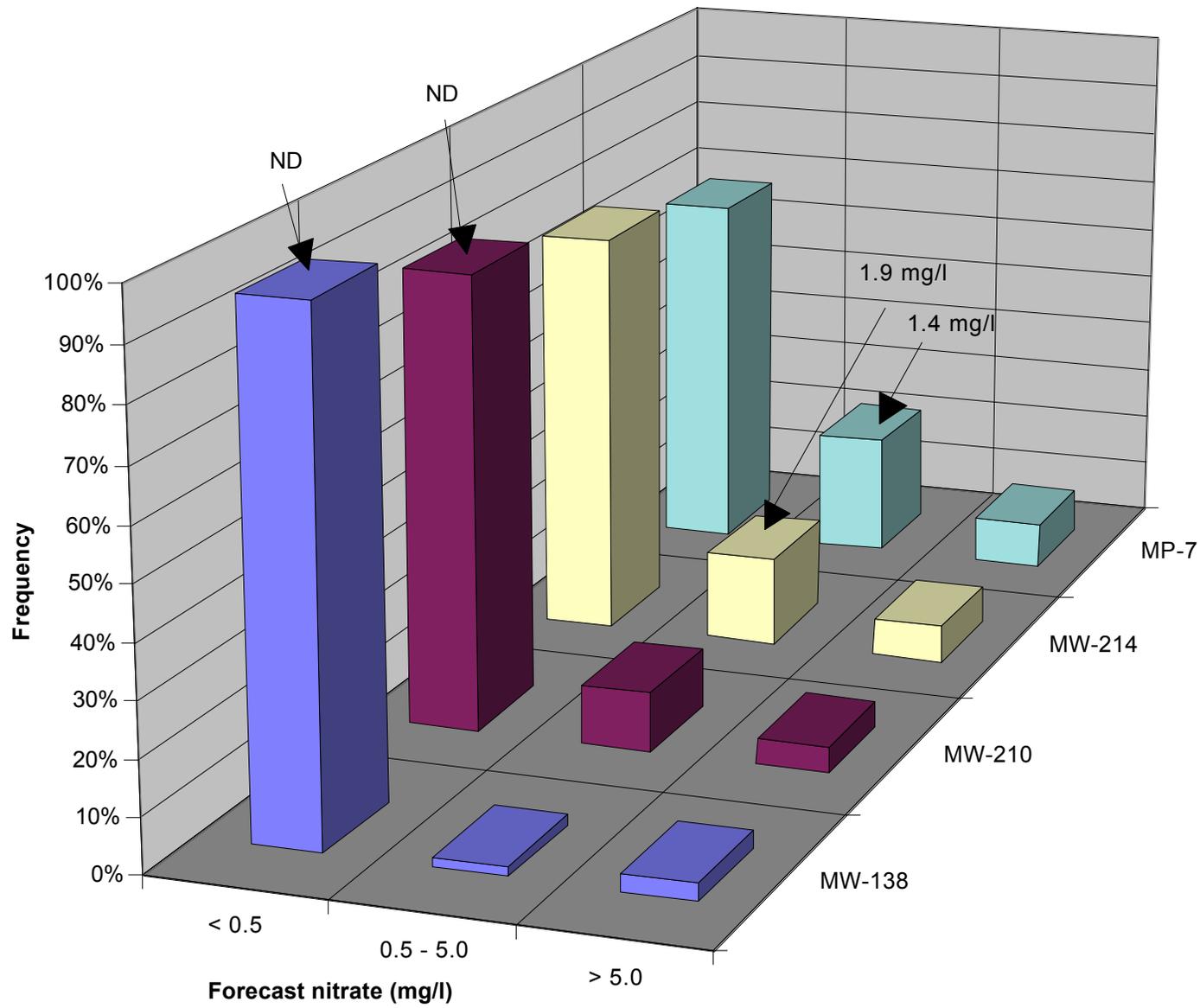


Figure B-6. Frequency distributions of forecast nitrate concentrations in selected monitoring wells.

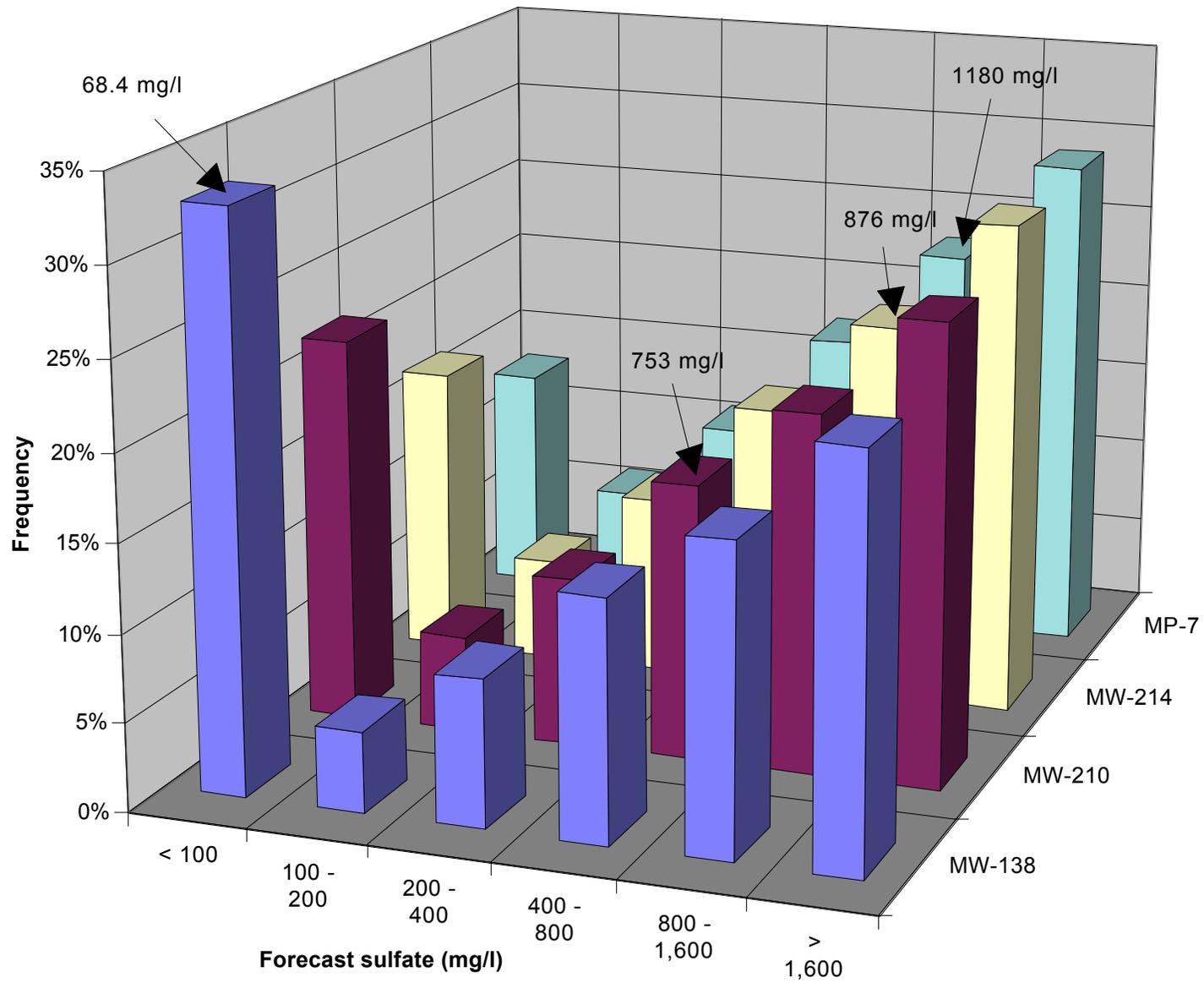


Figure B-7. Frequency distributions of forecast sulfate in selected monitoring wells.

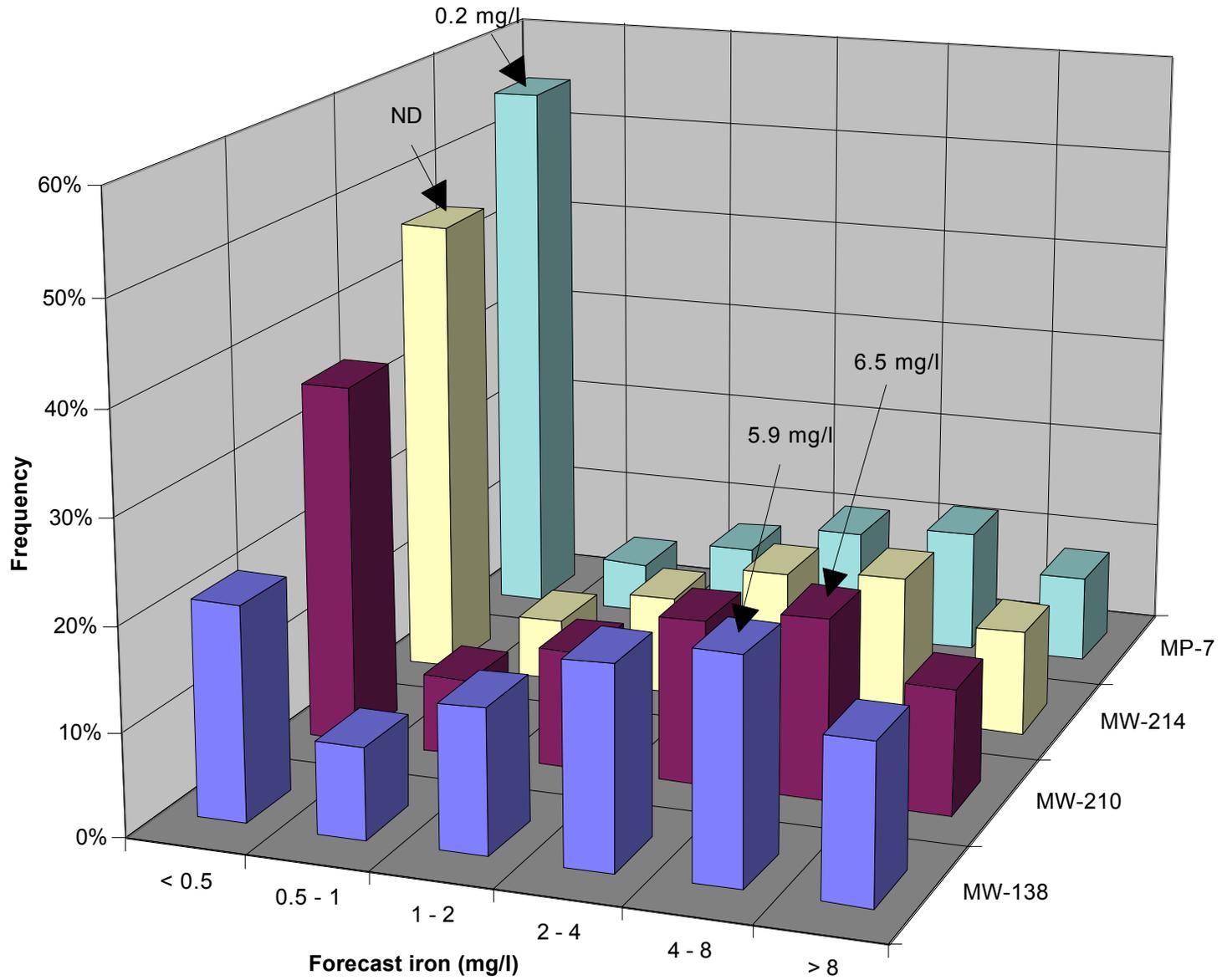


Figure B-8. Frequency distributions of forecast iron concentrations in selected monitoring wells.

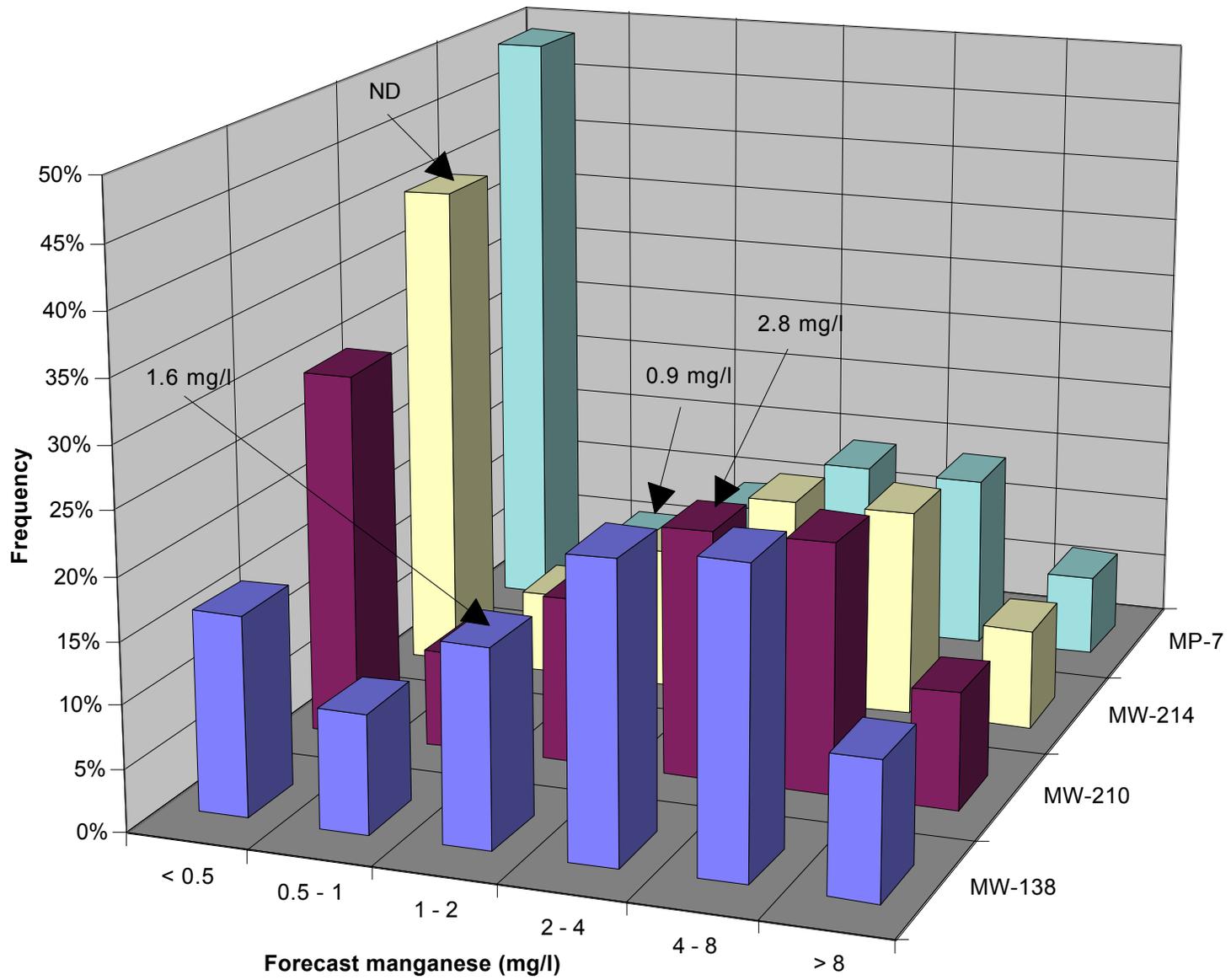


Figure B-9. Frequency distributions of forecast manganese concentrations in selected monitoring wells.

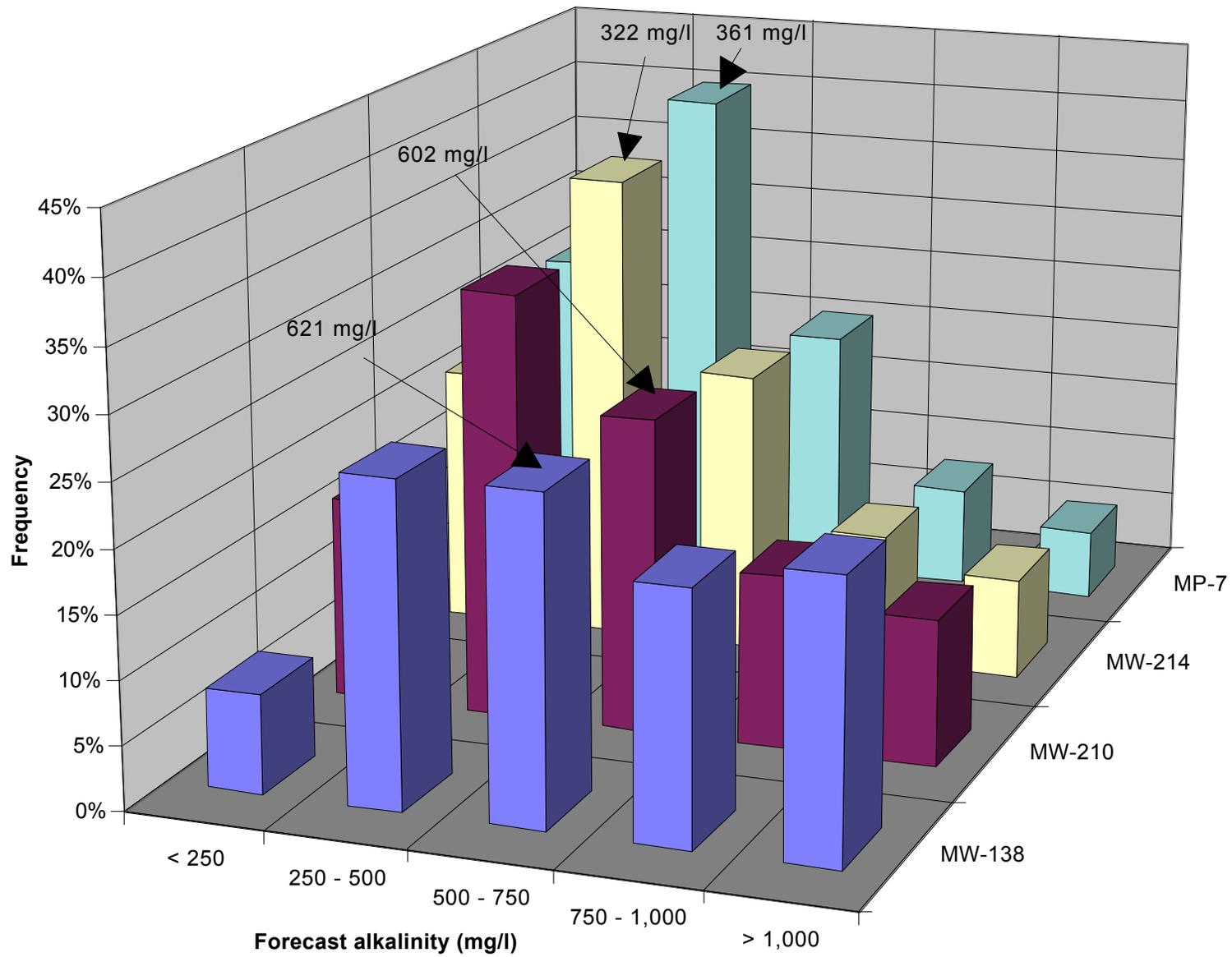


Figure B-10. Frequency distributions of forecast alkalinity concentrations in selected monitoring wells.

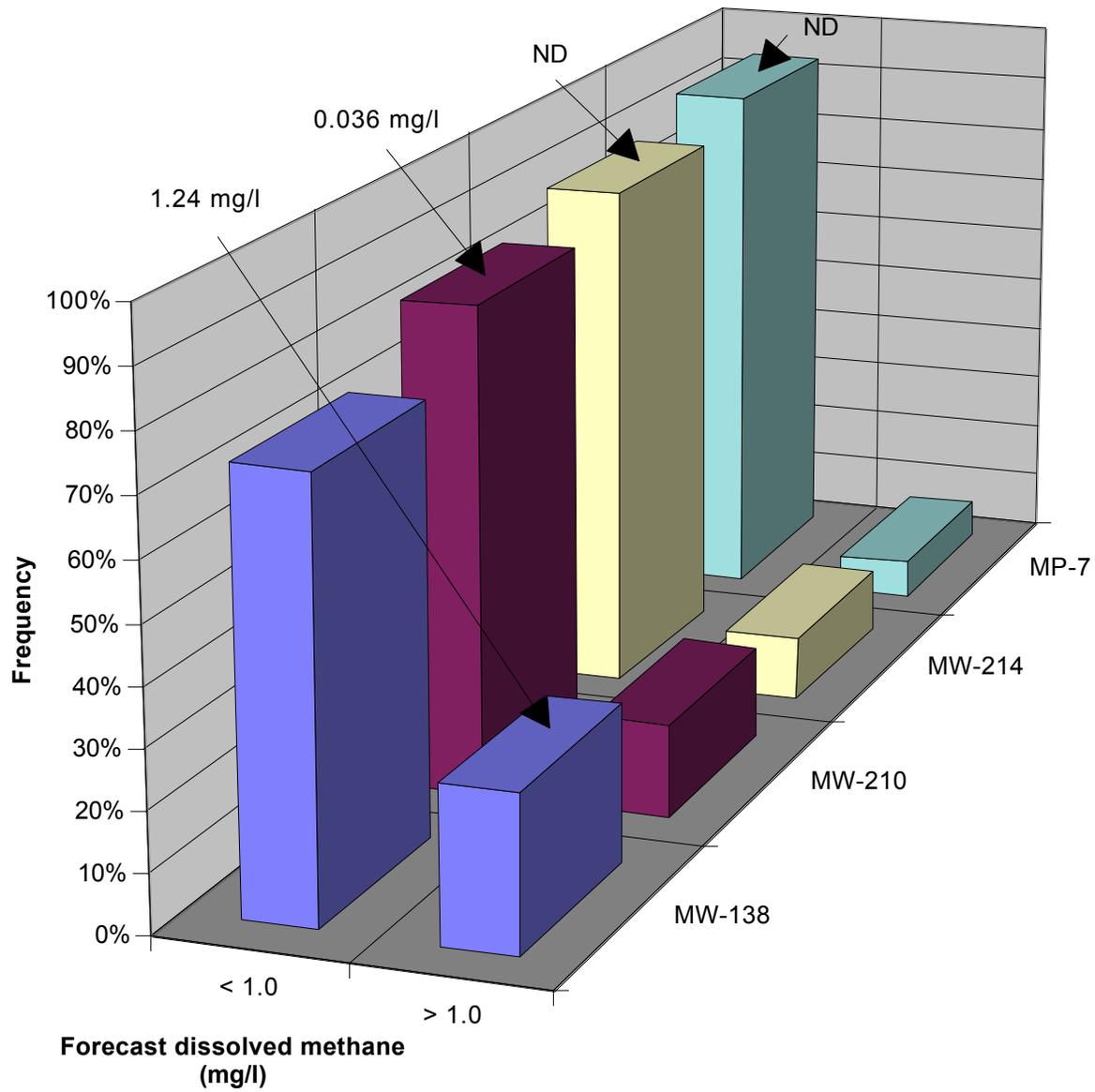


Figure B-11. Frequency distributions of forecast dissolved methane concentrations in selected monitoring wells.

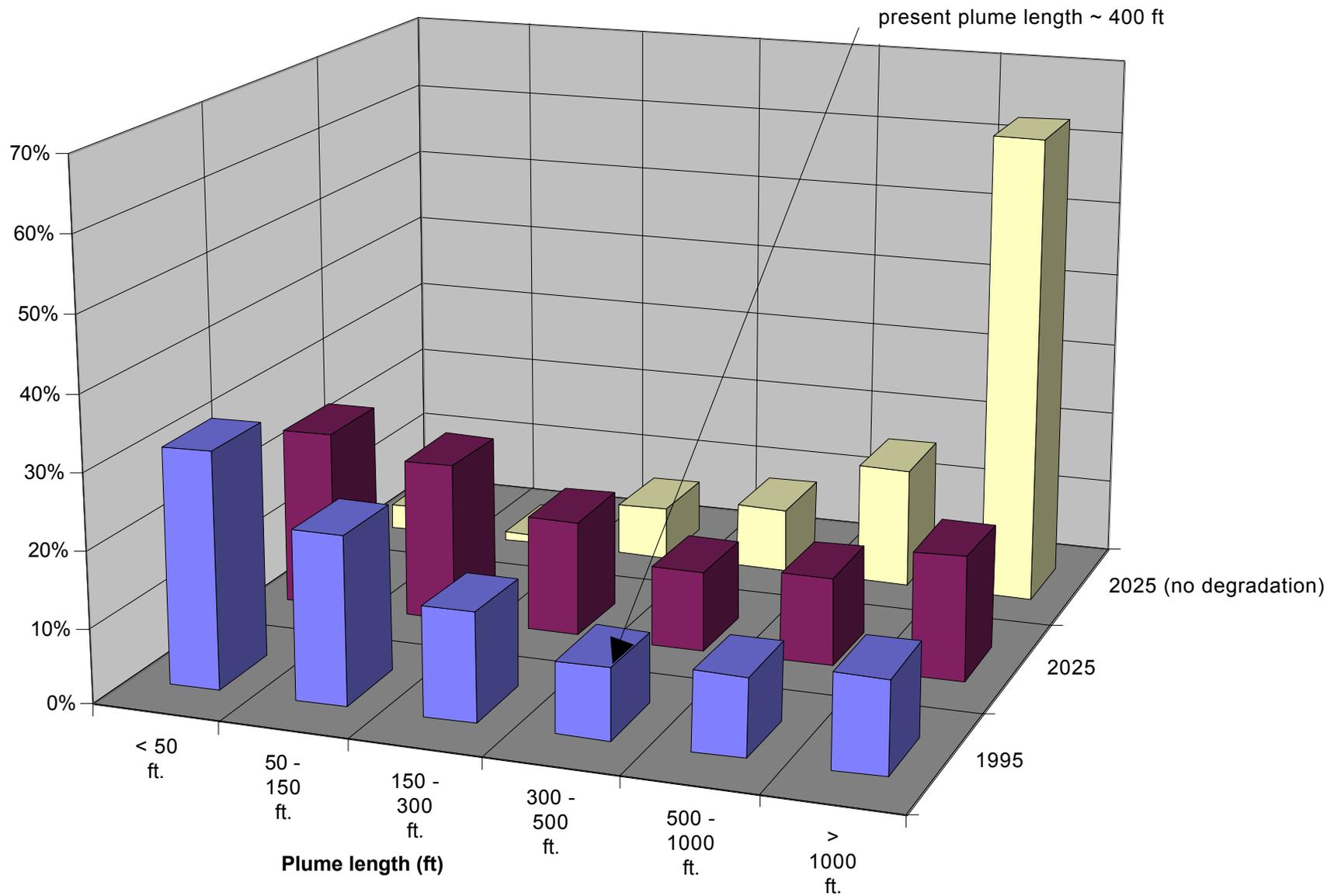


Figure B-12. Frequency distributions of forecast total BTEX plume lengths (as defined by the distance between the source and the 10 ppb contour) for 1995 and 2025.

Table B-1. Assumptions used in probability forecast mode.

| Parameter | Units | Distribution | Basis | Correlation |
|---|-------------------|--|---|---|
| C_0 , source concentration | mg/L | Normal. $\mu = 165$; $\sigma = 33$ (20% of μ) | Calculated total aqueous solubility of BTEX components from 87 octane gasoline composition (Kaplan and Galperin, 1996) and Raoult's law. Uncertainty addresses the possible bioattenuation of aliphatic hydrocarbons in addition to aromatics (increase source concentration) and source weathering (decreases source concentration). | None specified. |
| Y, source width | Ft | Normal. $\mu = 100$; $\sigma = 20$ (20% of μ) | Postulated. | None specified. |
| X_{source_i} , Y_{source_i} (one for each of the two source areas) | Ft | Normal. $\mu =$ Surveyed easting and northing coordinates; $\sigma = 50$ ft. | Site survey data, uncertainty postulated (location of leaks, NAPL pools, etc.). | None specified. |
| λ , decay coefficient | Day ⁻¹ | Lognormal. $\mu = 14\%$; $\sigma = 232\%$ (corresponding to a median value of 0.8%). | Postulated to span a large range of decay rates from essentially instantaneous to essentially unreactive; median value equivalent to those listed by Buscheck et al. (1996). | None specified. |
| K, hydraulic conductivity | Ft/day | Lognormal. $\mu = 10.0$; $\sigma = 20.6$. | Optimal fit of lognormal distribution to site data from aquifer tests (Parsons Engineering Science, 1996). | None specified. |
| ∇h , hydraulic gradient | – | Lognormal. $\mu = 3.75 \times 10^{-3}$; $\sigma = 2.49 \times 10^{-3}$. | Optimal fit of lognormal distribution to gradients calculated at site monitoring wells using a triangulation algorithm (see footnote ¹). | None specified (correlation between calculated gradients and hydraulic conductivities on a per well basis was not evident). |

¹ A probability distribution function for hydraulic gradient at the NSGS site was obtained by fitting planes to potentiometric surface elevation data from trios of monitoring wells, which were all within 300 ft of one another. The magnitude of the hydraulic gradient was then computed for each plane using vector analysis.

Table B-1. (Continued)

| Parameter | Units | Distribution | Basis | Correlation |
|---|-------------------|---|---|--|
| θ , gradient direction (used to rotate coordinate system) | Degree s | Normal. $\mu = 15$; $\sigma = 10$. | Site potentiometric surface map and plume isoconcentration contours (Parsons Engineering Science, 1996). | None specified. |
| ϕ , porosity | – | Lognormal. $\mu = 0.25$; $\sigma = 0.03$ (10% of μ). | Postulated. | None specified. |
| TOC, total organic carbon (soil) | mg/Kg | Weibull. Loc. = 367; Scale = 692.73; Shape = 1.36. | Optimal fit of Weibull distribution to TOC measurements from soil samples (Parson Engineering Science, 1996). | Inversely correlated (by rank) with background dissolved oxygen; $R = -0.5$ (postulated relationship). |
| ρ_b , soil bulk density | g/cm ³ | Normal. $\mu = 1.65$; $\sigma = 0.02$ (10% of μ). | Postulated. | None specified. |
| α_x ratio (ratio of longitudinal dispersivity to plume length scale, vt). | – | Lognormal. $\mu = 0.13$; $\sigma = 0.10$ (median = 0.10). | Postulated (based on the standard assumption that $\alpha_x \sim 10\%$ plume length). | None specified. |
| α_y ratio (ratio of transverse dispersivity to longitudinal dispersivity). | – | Lognormal. $\mu = 0.13$; $\sigma = 0.10$ (median = 0.10). | Postulated (based on the standard assumption that $\alpha_y \sim 10\% \times \alpha_x$). | None specified. |
| Background dissolved O ₂ | mg/L | Lognormal. $\mu = 1.25$; $\sigma = 2.74$. | Optimal fit of lognormal distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Inversely correlated (by rank) with soil TOC; $R = -0.5$ (postulated relationship). |
| Background effective Mn ²⁺ | mg/L | Beta. $\alpha = 0.99$; $\beta = 5.74$; Scale = 25.86. | Optimal fit of beta distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Correlated (by rank) with background effective Fe ²⁺ ; $R = +0.90$ (based on quantifiable trends in site data). |

Table B-1. (Continued)

| Parameter | Units | Distribution | Basis | Correlation |
|---|-------|--|---|---|
| Background NO ₃ ⁻ | mg/L | Lognormal. μ = 4.13; σ = 17.02. | Optimal fit of lognormal distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Correlated (by rank) with background SO ₄ ²⁻ ; R = +0.33 (based on quantifiable trends in site data). |
| Background effective Fe ²⁺ | mg/L | Beta. α = 0.77; β = 4.71; Scale = 30.00. | Optimal fit of beta distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Correlated (by rank) with background effective Mn ²⁺ ; R = +0.90 (based on quantifiable trends in site data). |
| Background SO ₄ ²⁻ | mg/L | Exponential. Rate = 7.19 x 10 ⁻⁴ | Optimal fit of beta distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Correlated (by rank) with background NO ₃ ⁻ (R = +0.33) and background alkalinity; R = +0.67 (based on quantifiable trends in site data). |
| Background alkalinity | mg/L | Lognormal. μ = 373; σ = 266. | Optimal fit of beta distribution to site groundwater quality data (Parsons Engineering Science, 1996). | Correlated (by rank) with background SO ₄ ²⁻ ; R = +0.67 (based on quantifiable trends in site data). |
| t, time elapsed between introduction of source and groundwater quality sample | Years | Normal. μ = 30; σ = 2.5 (truncated at 30 years). | Postulated (assuming source became active after tanks were installed in 1965). | None specified. |

Table B-2. Forecast BTEX concentration sensitivity to assumptions.

| Well | Decay coefficient (%) | Hydraulic conductivity (%) | Hydraulic gradient (%) | α_x -to-plume length ratio (%) | Northing coordinate of nearest source (%) |
|--------|-----------------------|----------------------------|------------------------|---------------------------------------|---|
| MW-138 | 50 | 37 | 8 | 1 | 4 |
| MW-210 | 42 | 45 | 9 | 2 | <1 |
| MW-214 | 39 | 48 | 10 | 2 | <1 |
| MP-7 | 36 | 50 | 10 | 3 | <1 |

Table B-3. Forecast geochemical indicator sensitivity to parameter assumptions.

| Parameter | MW-138 (close to source) | MP-7 (distant from source) |
|-------------------------------|---|---|
| O ₂ | Not present | Hydraulic conductivity (74%) Gradient (13%) Background O ₂ (8%) α_x -ratio (2%) Soil TOC (2%) ^a |
| Mn ²⁺ | Background Mn ²⁺ (55%) Background Fe ²⁺ (44%) ^a | Hydraulic conductivity (60%) Background Mn ²⁺ (15%) Background Fe ²⁺ (12%) ^a Gradient (10%) α_x -ratio (1%) |
| NO ₃ ⁻ | Not present | Hydraulic conductivity (70%) Background NO ₃ ⁻ (12%) Gradient (12%) α_x -ratio (2%) Background SO ₄ ²⁻ (1%) ^a |
| Fe ²⁺ | Background Fe ²⁺ (56%) Background Mn ²⁺ (44%) ^a | Hydraulic conductivity (65%) Background Fe ²⁺ (11%) Gradient (11%) Background Mn ²⁺ (9%) ^a α_x -ratio (1%) |
| SO ₄ ²⁻ | Background SO ₄ ²⁻ (64%) Background alkalinity (26%) ^a Background NO ₃ ⁻ (7%) ^a Decay coefficient (1%) | Background SO ₄ ²⁻ (65%) Background alkalinity (28%) ^a Background NO ₃ ⁻ (7%) ^a |
| CH ₄ | Background SO ₄ ²⁻ (58%) Background alkalinity (25%) ^a Background NO ₃ ⁻ (7%) ^a Decay coefficient (4%) C ₀ (2%) α_x -ratio (1%) Gradient direction (1%) | Not present |

Table B-3. (Continued)

| Parameter | MW-138 (close to source) | MP-7 (distant from source) |
|------------|--|--|
| Alkalinity | Background alkalinity (49%) | Background alkalinity (60%) |
| | Background SO_4^{2-} (33%) ^a | Background SO_4^{2-} (28%) ^a |
| | Decay coefficient (7%) | Hydraulic conductivity (7%) |
| | Background NO_3^- (4%) ^a | Background NO_3^- (3%) ^a |
| | C_0 (2%) | |
| | Gradient direction (1%) | |
| | Source width (1%) | |
| | α_x -ratio (1%) | |

* Indicates a correlated assumption, where the implied parameter sensitivity may be the result of association with another influencing parameter rather than representing a real effect.

Appendix C

Uncertainty Analyses and Risk Assessment of Volatile Fuel Hydrocarbon Flux in the Vadose Zone Using Probabilistic Forecasts

Appendix C

Uncertainty Analyses and Risk Assessment of Volatile Fuel Hydrocarbon Flux in the Vadose Zone Using Probabilistic Forecasts

C-1. Introduction

Aside from an ingestion risk potential via contaminate groundwater, fuel hydrocarbon compounds (FHCs) may pose a significant vapor inhalation risk to human receptors at the surface, near points of release. To evaluate the potential FHC inhalation hazard, the vapor source, migration pathway, and the presence of probable receptors must all be considered (Kaplan and Garrick, 1981). In particular, variability and uncertainty in physical and chemical parameters affecting FHC vapor transport must be addressed. These include the total FHC mass, distance from the source to the ground surface, the soil water content, soil porosity, soil organic carbon content, and the degradation potential of the FHCs, all of which are highly variable and uncertain in the complex vadose zone environment. Uncertainties pertaining to human health impact (e.g., exposure time, distance from vapor flux points, degree of enclosure) also must be addressed to permit an integrated analysis of the associated risk.

To address these uncertainties, a probabilistic modeling approach has been developed to provide a means of forecasting vapor transport and exposure. This approach involves the application of a Monte Carlo simulation technique to several analytical solutions of the diffusive transport equation for vapors. The 95th and 99th percentile flux results are employed to quantify risk using a health impact equation. Benzene, the most toxic of the FHCs constituents, is used as the marker compound in this evaluation. This model has been applied to the hydrocarbon release site associated with the North-South Gas Station (NSGS) at Travis Air Force Base (TAFB) in Fairfield California. Because air sampling has not been conducted at the potential receptor locations on the site, the forecasts generated are intended as screening level tools to provide regulatory personnel and site stakeholders insights into data requirements and potential health impacts associated with vapor migration at NSGS site.

C-2. Modeling of Vapor Transport

In environments characterized by minimal vertical recharge, contaminant transport through the vadose zone is primarily a diffusive process. The Laplace transform technique has been successfully employed in several studies to find mathematical solutions to this problem, assuming a semi-infinite porous medium (Jury et. al., 1983; 1984a,b,c; and 1990).

According to Jury et al. (1990), the cumulative vapor flux at the surface, assuming a zero boundary layer thickness, or infinite mass transfer coefficient, with no advection, can be expressed as:

$$V_c^b(\infty) = \frac{C_g}{R_g} \left(\frac{D_{eff}}{\lambda} \right)^{1/2} \exp \left[-L \left(\frac{\lambda}{D_{eff}} \right)^{1/2} \right] \left\{ 1 - \exp \left[-W \left(\frac{\lambda}{D_{eff}} \right)^{1/2} \right] \right\} \quad \text{Eq. C-1}$$

where L refers to the distance from ground surface to the NAPL, λ the first-order decay coefficient, D_{eff} the effective diffusion coefficient, and W the thickness of the NAPL layer.

The effective gas diffusion coefficient is given by,

$$D_{g,eff} = \frac{D_g}{R\tau} \quad \text{Eq. C-2}$$

where R_g refers to the effective contaminant retardation due to interphase partitioning and τ the material tortuosity. It may be shown from simple mass balance and partitioning relationships (i.e., Henry's law partitioning, the linear adsorption isotherm) that,

$$C_T = C_g \left(\theta_g + \frac{\theta_l}{H} + \frac{\rho_b K_d}{H} \right) = R_g C_g \quad \text{Eq. C-3}$$

where θ_1 is the volumetric water content of the soil, θ_g the vapor content, H the dimensionless Henry's Law Constant, ρ_b the soil bulk density, and K_d is the distribution coefficient. The tortuosity, τ , for gaseous diffusion in air-filled pore spaces (neglecting entrapped water), is given by the Millington (1959) equation, as corrected by Falta et al. (1992),

$$\tau = \frac{\phi^2}{\theta_g^3} \quad \text{Eq. C-4}$$

where ϕ refers to the soil porosity. Accounting for contaminant diffusion through the aqueous phase, the effective gaseous diffusion coefficient may be given as,

$$D_{eff} = \frac{\theta_g^3 D_g H + \theta_l^3 D_l}{\phi^2 (\rho_b K_d + \theta_l + \theta_g H)} \quad \text{Eq. C-5}$$

where D_g and D_a refer to the free gaseous and aqueous diffusion coefficients, respectively.

The solution given by Eq. C-1 is an approximation for cumulative flux over an infinite time period; providing a reasonable approximation for cumulative exposure in many situations. However, it does not provide an estimate of the actual time required for the removal of the contaminants from the subsurface via diffusion. Such a time period may be greater than or less than the actual exposure duration. However, the error associated with this problem will always produce conservative results.

Finally, consider that the true mass flux is three dimensional, and will follow torturous paths based on local hydrostratigraphy. Thus, the total flux that reaches the surface will certainly be less than that stated for the "straight-line" or unidirectional path. Therefore, the use of a unidirectional mass flux model for contaminant vapor transport is also a conservative approximation.

Physical constants and distributions used in the Monte Carlo simulation are given on Table C-1.

C-3. Receptors

Base residences exist in the vicinity of the North Gas Station, forming a semi-circle arc approximately 300 feet upgradient of the northern plume boundary. Air Force personnel and their families typically reside in these dwellings for periods of six months to two years. In addition, Building 175, one of three full-time manned fire stations on the TAFB site, is located approximately 150 feet east of the South Gas Station.

There are base residences ranging from east to the north in a semi-circle arc 300 feet from the NGS, all upgradient of the plume upper boundary (Personal Communication, Mr. Wilford Day TAFB Environmental Management, December 2, 1996). According to Ms. Millissa Laven (Personal Communication, TAFB Housing Office, December 2, 1996) family residence times for these buildings are from a minimum of 6 months to a maximum of 6 years, with an average stay of 2 to 3 years. Using these numbers, a log-normal distribution may be derived (e.g., 6 months represents the 0.1 percentile and 6 years represents the 99 percentile of the exposure duration (ED). The above percentiles result in an average residence or ED time of 2.29 years and a standard deviation of 1.11 years. No more than two children would be located in these residences; most families are young, and the children will be in the early developmental stage. Typical activity patterns may be used. Housing types are mixed between slab foundation and crawl-space type foundations. For these families, the predicted vacation time or time away from home per year is two weeks, plus a maximum of 10 weekends away from home, making an exposure frequency (EF) of 330 to 350 days/year.

Building 175, one of three full-time manned TAFB Fire Stations, is a one-story structure with a slab foundation, constructed of wood and brick and is located approximately 150 feet east of the South Gas Station. It accommodates 4 to 5 persons/day approximately 4 to 5 months/year. We may derive from this a triangular distribution for the EF of 120 to 150 days/year. Some firefighters at these stations are short-term employees, while others are career employees, with a 20 to 30 year expected lifetime employment. Because career employees' jobs are rotated within the the TAFB Fire Stations (Personal Communication, Mr. William Nowlin, TAFB Hazardous Materials Coordinator, December 2, 1996), this rotation may reduce the lifetime exposure between one-half to one-third of the expected lifetime employment. The estimated ED then becomes the product of the "rotation period" (a normal distribution within the bounds of the 5th and 95th percentiles of 0.33 to 0.5) and the "career period" (a normal distribution within the bounds of the 5th and 95th percentiles of 20 to 30 years). The ED derived from this is approximately normal with a mean of 10.4 years and a standard deviation of 1.8 years.

Table C-2 shows the input parameters for the Monte Carlo simulation associated with living in the general area of the service stations at TAFB.

C-4. Risk Analysis

Risk is determined based on the amount of some toxic material which may cause adverse health effects. The Target Risk (TR) may be defined as,

$$TR = 1 - \exp(-LADD \times CPF) \quad \text{Eq. C-6}$$

$$\cong LADD \times CPF$$

where $LADD$ is the Lifetime Average Daily Dose (mg/kg-day) and CPF is the Cancer Potency Factor (kg-day/mg). This may be expanded further:

$$LADD = C \times E \quad \text{Eq. C-7}$$

where C is the concentration, and E is exposure factor representing duration, pathway, frequency, etc. Consider, as an example, the appropriate exposure definition for the inhalation:

$$E = \frac{EF \times ED \times IR}{BW \times AT} \quad \text{Eq. C-8}$$

where EF is the receptor's exposure frequency (days/year), ED the duration of time the receptor is exposed (years), IR the inhalation rate of air (L/day), BW the receptor's average body weight impacted by the contaminant (kg), and AT_c the averaging time for carcinogens (years). The target risk may then be defined as:

$$TR = C_g \times E \times CPF \quad \text{Eq. C-9}$$

or,

$$TR = \frac{C_g \times IR \times EF \times ED \times CPF}{BW \times AT} \quad \text{Eq. C-10}$$

Equation C-1 describes the cumulative vapor flux over an infinite time period. Translating this result into a yearly average "mixing zone concentration" at the surface requires that the cumulative flux be divided by the averaging time, AT , as well as a mixing zone height, d , assumed to be on the order of 2 m:

$$\dot{C}_g = \frac{V_o^b(\infty)}{AT \cdot d} \quad \text{Eq. C-11}$$

A Monte Carlo simulation, utilizing the Crystal Ball add-in package (Decisioneering, 1996) for Microsoft Excel (1993) was used to forecast target risk estimates. The results are shown on Table C-2. Target risk estimates are forecast at well below 10^{-6} at the 99th percentile for all receptors for the high likelihood distribution of degradation rates. For the low likelihood degradation rate distribution, target risk estimates were at 10^{-6} below the 96th percentile for the fire station, and well below 10^{-6} at the 99th percentile for the residences. Sensitivity analyses indicate that the largest contribution to variance in the above analysis is uncertainty in the contaminant degradation rate, followed by source mass per unit area and the water content of the soil. Organic carbon content contributed only slightly to the total variance.

The estimates for risk are derived using a conservative one-dimensional model, one which assumes that there is a direct path between the source and the receptor. For the residential areas, this source is the North Gas Station; for the Fire Station, this source is the South Gas Station. As such, the risk estimates are likely to be highly conservative because the nature of vapor diffusion toward the receptors is likely to be a radial geometry as opposed to uni-directional. Such a radial pattern would tend to dilute the flux over a much wider area.

C-7. References

- ASTM. 1995. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (E 1739-95). American Society for Testing and Materials, West Conshohocken, PA.
- Brainard, J. and Burmaster, D. E. 1992. Bivariate Distributions for Height and Weight of Men and Women in the United States. *Risk Analysis*. **12**, 267-275.
- Decisioneering, Inc. 1993. Crystal Ball Ver. 3.0 Users Manual. Denver, Co. Decisioneering, Inc.
- DeVaull, G. E., J. B. Gustafson, and J. P. Salanitro. 1996. Benzene Degradation in Vadose Zone Soils During Vapor Transport: First-Order Rate Constants, Shell Oil, Aug. 22, 1996.
- Falta, R. W., K. Pruess, I. Javandel, and P. A. Witherspoon. 1992. Numerical Modeling of Steam Injection for the Removal of Nonaqueous Phase Liquids from the Surface. I: Numerical Formulation. *Water Resources Research*. **28**, 433449.
- Finley, B., D. Proctor, P., Scott, N., Harrington, D., Paustenbach, and P. Price. 1994. Recommended Distributions for Exposure Factors Frequently Used in Health Risk Assessment. *Risk Analysis*. **12**, 533-553.
- Howard, P. H. 1991. Handbook of Environmental Degradation Rates. Lewis Publishing, Chelsea, MI.
- Johnson, P. C., B. H. Marvin, and D. L. Byers. 1989. Estimates for Hydrocarbon Vapor Emissions Resulting from Service Station Remediations and Buried Gasoline-Contaminated Soils in *Petroleum Contaminated Soils*, Vol. 3. P. T. Kosteki and E. J. Calabrese, Eds. Lewis Publishers, Chelsea, MI.
- Jury, W. A., W. F. Spencer, and W. J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: I. Model Description. *Journal of Environmental Quality*. **12**, 558-564.
- Jury, W. A., W. J. Farmer, and W. F. Spencer. 1984a. Behavior Assessment Model for Trace Organics in Soil: II. Chemical Classification and Parameter Sensitivity. *Journal of Environmental Quality*. **13**, 567-572.
- Jury, W. A., W. F. Spencer, and W. J. Farmer. 1984b. Behavior Assessment Model for Trace Organics in Soil: III. Application of Screening Model. *Journal of Environmental Quality*. **13**, 573-579.
- Jury, W. A., W. F. Spencer, and W. J. Farmer. 1984c. Behavior Assessment Model for Trace Organics in Soil: IV. Review of Experimental Evidence. *Journal of Environmental Quality*. **13**, 580-586.
- Jury, W. A. 1985. Spatial Variability of Soil Physical Parameters in Solute Migration: A Critical Literature Review. *Electric Power Research Institute*. EA-4228, Palo Alto, CA, September 1985.
- Jury, W. A., D. Russo, G. Steile, and H. E. Abd. 1990. Evaluation of Volatilization by Organic Chemicals Residing Below the Soil Surface, *Water Resources Research*. **26**, 13-20.

- Kaplan S. and Garrick B. J. 1981. On the Quantitative Definition of Risk. *Risk Analysis*. **1**, 11–27.
- Layton, D. W. 1993. Metabolically Consistent Breathing Rates for Use in Dose Assessments. *Health Physics*. **64**, 23–36.
- Millington, R. J. 1959. Gas Diffusion in Porous Media. *Science*. **130**, 100–102.
- Parsons Engineering Science. 1996. Final Treatability Study to Evaluate Intrinsic Remediation at the North and South Gas Stations, Vol. 2: Appendices. Travis Air Force Base, CA. Prepared for the Air Force Center for Environmental Excellence, Brooks Air Force Base, TX.
- U.S. Environmental Protection Agency (EPA). 1989. Exposure Factors Handbook. U.S. Environmental Protection Agency, Exposure Assessment Group, Office of Health and Environmental Assessment. EPA/600/8-89/043.

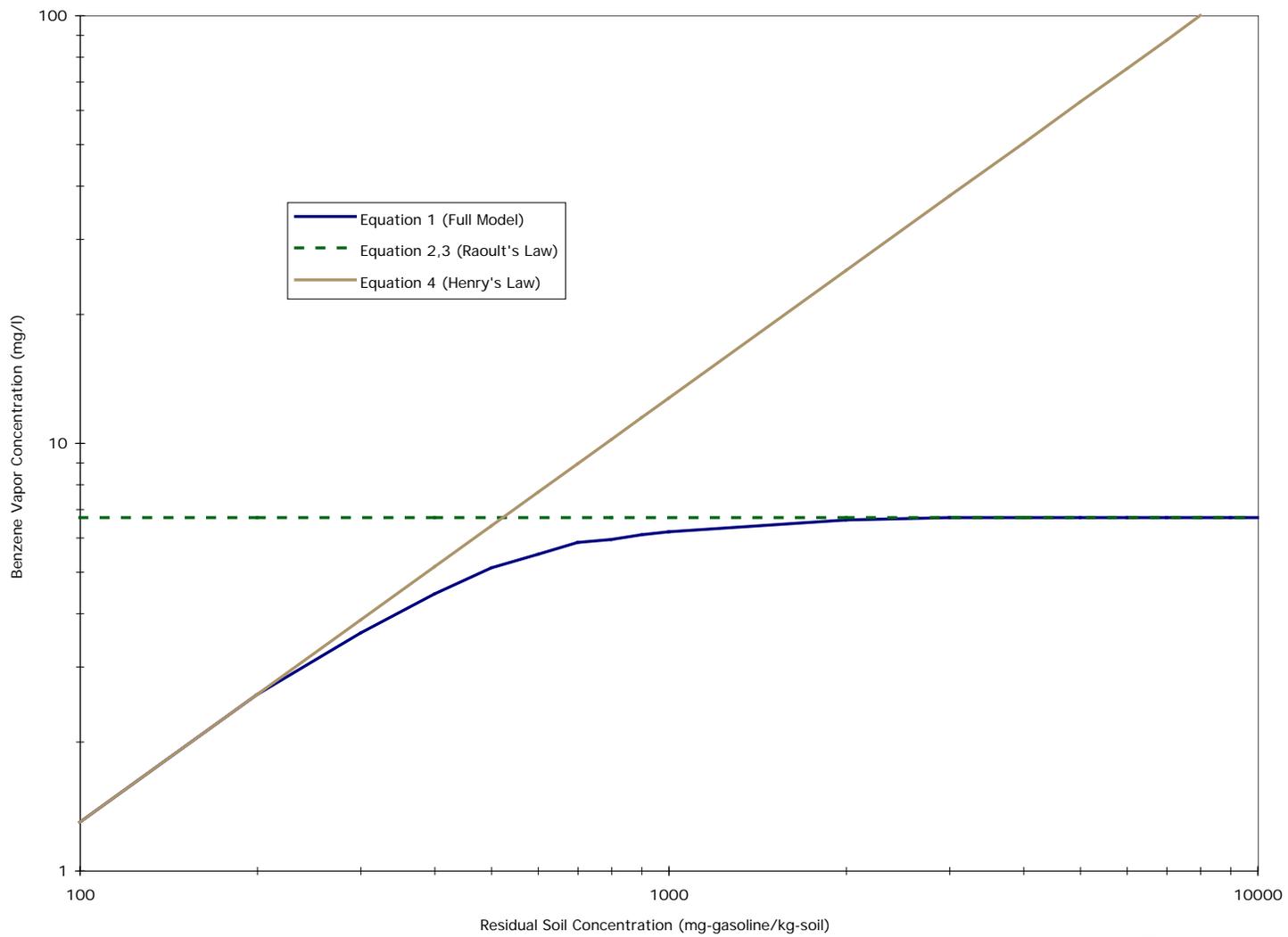


Figure C-1. Concentration prediction models.

Table C-1. Input parameters and their values for the calculation of vapor inhalation risk.

| Parameter | Probability distribution | Basis |
|--|--|---|
| Body Weight (BW) | Normal. $m = 71$ kg; $s.d. = 15.9$ kg | Brainard and Burmaster (1992) |
| Exposure Duration (ED) | Normal. | Best professional judgment based on site specific information |
| • Fire Station | $m = 10.4$ yr; $s.d. = 1.8$ yr | |
| • Residences | Lognormal. | |
| • Residences | $m = 2.3$ yr; $s.d. = 1.1$ yr | |
| Exposure Frequency (EF) | Triangular. | Best professional judgment based on site specific information |
| • Fire Station | 120, 145, 150 days | |
| • Residences | 330, 345, 350 days | |
| Inhalation Rate (IR) | Lognormal. $m = 12.06$ L/day; $s.d. = 2.55$ L/day | Layton (1993) |
| Cancer Potency Factor (CPF) of Benzene | Point. 0.10 kg day/mg | Proposition 65, Finley et al. (1994) |
| Averaging Time (AT) | Point. 70 yr | U.S. EPA (1989) |
| Distance to receptor (L) | Point. | Best professional judgment based on site specific information |
| • Fire station | 150 ft (46 m) | |
| • Residences | 300 ft (92 m) | |
| Chemical concentration (C_0) | | Raoult's Law |
| Source Thickness (W) | Lognormal. $m = 2.85$ cm; $s.d. = 2.9$ cm | Best professional judgment |
| Air Mixing Zone Height (d) | Point. 6 ft (183 cm) | U.S. EPA (1989); Johnson et al. (1989) |
| Porosity (ϕ) | Normal. $m = 0.37$; $s.d. = 0.042$ (dimensionless) | Jury (1985) |
| Volumetric Water Content (θ_l) | Normal. $m = 0.189$; $s.d. = 0.0284$ $\theta_l \leq \phi$ (dimensionless) | Based on site data (Parsons Engr., 1996) |
| Volumetric Air Content (θ_g) | function of water content and porosity - $\theta_g = \phi - \theta_l$ (dimensionless) | Function |
| Diffusivity (D_g) of Benzene in air | Point. 9.3×10^{-2} cm ² /s | ASTM (1995) |
| Diffusivity (D_l) of Benzene in water | Point. 1.1×10^{-5} cm ² /s | ASTM (1995) |
| Henry's Law Constant (H) of Benzene | Point. 0.223 (dimensionless) | ASTM (1995) |
| Total Organic Carbon (TOC) - soil | Lognormal. $m = 1001$ mg/kg; $s.d. = 470$ mg/kg | Based on site data (Parsons Engr., 1996) |
| Bulk soil density (clay loam and sandy loam) | Normal. $m = 1.41$ mg/kg; $s.d. = 0.08$ mg/kg | Jury (1985) |
| Degradation rate (λ) | Lognormal. | Best professional judgment based on site specific information; Howard (1991); DeVaull et al. (1996) |
| Low likelihood | $m = 9.95 \times 10^{-8}$ /s, $s.d. = 2.31 \times 10^{-7}$ /s; | |
| High likelihood | $m = 9.95 \times 10^{-7}$ /s, $s.d. = 2.31 \times 10^{-6}$ /s | |

Table C-2. Target risk values for potential receptors at the TAFB site as a function of degradation rates (λ).

| TAFB target risk areas | 99th percentile high likelihood (λ) | 99th percentile low likelihood (λ) | 96th percentile low likelihood (λ) |
|------------------------|---|--|--|
| Fire Station | $< 10^{-6}$ | $< 3 \times 10^{-5}$ | $< 10^{-6}$ |
| Residences | $< 10^{-6}$ | $< 10^{-6}$ | $< 10^{-6}$ |

Attachment A
A Critique of a Steady-State Analytical Method for
Estimating Contaminant Degradation Rates

Attachment A

A Critique of a Steady-State Analytical Method for Estimating Contaminant Degradation Rates

Abstract

Contaminant degradation rates are often estimated from monitoring well data using regression analysis based on steady-state analytical models as a simple screening technique. Such an approach assumes one-dimensional solute transport in the presence of a continuous boundary concentration and a uniform first-order degradation coefficient. It must be recognized that this type of analysis is easily subject to misinterpretation, particularly when few monitoring points are used. This is because the dispersive nature of solute transport can produce concentration profiles which closely resemble those associated with a degrading contaminant even in the absence of any transformation processes. Furthermore, sensitivity analyses indicate that the uncertainties in the effective contaminant transport velocity dominate the variance in predicted degradation rates above all other factors. Such sensitivity of a chemical/biological parameter to a physical parameter contributes to the likelihood of spurious degradation rate estimates.

Fuel hydrocarbons and other common organic contaminants are frequently subject to biodegradation processes in groundwater environments. If the rate of biotransformation of a given contaminant at a site is idealized as being uniform in time and space, then, in the presence of a continuous source (e.g., a residual pool of free product), the plume associated with the dissolved contaminant will achieve a steady-state condition. This occurs as a result of a mass balance between contaminant influx from the source (e.g., free product dissolution) and contaminant loss through transformation reactions, integrated across the spatial extent of the plume. The contaminant transformation rate, therefore, will play a major role in determining the extent to which such a steady-state contaminant plume will extend in the direction downgradient from the source.

Buscheck and Alcantar (1995) suggested that the steady-state distribution of contaminant concentrations downgradient of a continuous source can be used to estimate transformation rates. Such rate information is very useful, for example, in the assessment of the transport of a hazard between its source and a risk receptor, and in determining the required corrective action. Assuming a first-order decay coefficient as an approximation for the biotransformation of the contaminant, Buscheck and Alcantar (1995) showed, for a one-dimensional idealization, that the degradation rate λ may be given by,

$$\lambda = \frac{v_c}{4\alpha_x} \left\{ \left[1 + 2\alpha_x \left(\frac{k}{v_x} \right) \right]^2 - 1 \right\} \quad (1)$$

where v_c is the contaminant velocity along the x -direction (adjusted for retardation), α_x the longitudinal dispersivity, and k/v_x the slope of a line fit to data points on a log contaminant concentration (x -axis) versus distance downgradient along the plume centerline. By plotting log contaminant concentrations in various wells downgradient from the source as a function of distance and fitting a line through the data using linear regression, one could, in principle, estimate a first-order degradation rate if the fit is reasonably good.

This technique has become widely used to estimate degradation rates of dissolved fuel hydrocarbons associated with leaking underground fuel tanks (LUFTs). However, it must be recognized that a significant potential for misinterpretation of results exists in applying this technique. This is because simple dispersive processes (macroscale mechanical mixing and molecular diffusion) produce concentration distributions which, ideally, decline with distance from a continuous source as determined by an error function term (even in the absence of any solute degradation). In many instances, particularly when using only a small number of data points (i.e., monitoring wells), it is often possible to fit a straight line through log concentration versus distance data with a high degree of correlation even when degradation is not an important process. Therefore, it is possible to derive estimated degradation rates which are entirely spurious.

The method of Buscheck and Alcantar (1995) represents an inverse solution technique. Inverse solutions by their nature are particularly sensitive to the initial and boundary conditions associated with the problem. This sensitivity is increased through measurement and modeling errors. Mathematically, such problems are considered ill-posed due to a lack of uniqueness and stability resulting from small changes in the input data. The potential for misinterpretation of the inverse problem when using the method of Buscheck and Alcantar (1995) is best illustrated by example. Consider the total BTEX (benzene/toluene/ethylbenzene/xylene) concentrations measured in three monitoring wells located downgradient of a LUFT site in northern California (Table 1).

Table 1. BTEX concentrations as a function of distance from source.

| Well | Distance downgradient (m) | Total BTEX ($\mu\text{g/L}$) |
|---------|---------------------------|--------------------------------|
| Well #1 | 0 | 67,000 |
| Well #2 | 26 | 23,500 |
| Well #3 | 113 | 4,095 |

Assuming a retarded contaminant velocity of 6.1 m/year and a longitudinal dispersivity of 2.7 m (equal to approximately 1% of the length of the BTEX plume at the site), a straight line fit through the monitoring well data yields a slope of 0.023 with correlation given by $R^2 = 0.974$ (Figure Attach A-1). Substitution of this value into Eq. (1) yields an estimated degradation rate of 0.04% day⁻¹. Now consider an alternate scenario. Suppose that the site is modeled by the familiar Domenico (1987) solution to the two-dimensional advective-dispersive transport equation with a continuous line source,

$$C(x, y, t) = \left(\frac{C_0}{4} \right) \exp \left\{ \left(\frac{x}{2\alpha_x} \right) \left[1 - \left(1 + \frac{4R\lambda\alpha_x}{v} \right)^{1/2} \right] \right\} \quad (2)$$

$$\cdot \operatorname{erfc} \left[\frac{x - \frac{v}{R} t (1 + 4R\lambda\alpha_x / v)^{1/2}}{2 \left(\alpha_x \frac{v}{R} t \right)^{1/2}} \right] \cdot \left\{ \operatorname{erf} \left[\frac{(y + Y/2)}{2(\alpha_y x)^{1/2}} \right] - \operatorname{erf} \left[\frac{(y - Y/2)}{2(\alpha_y x)^{1/2}} \right] \right\}$$

where C_0 refers to the source concentration (constant with time), α_y the transverse dispersivity, v the groundwater pore velocity, R the retardation coefficient, Y the width of the line source, t the monitor time, and x and y the Cartesian coordinates of the monitor point relative to the source. Assuming a value of $67,000 \mu\text{g/L}$ for C_0 , a source width of 15 m, a flow velocity of 12.2 m/year (corresponding to a contaminant velocity of 6.1 m/year when $R = 2.0$), and various longitudinal dispersivity values (2.7 m, 13.5 m, and 27 m, corresponding to 1%, 5% , and 10% of the approximate plume length, respectively), with the transverse dispersivity equal to 10% of the longitudinal value, and a first-order decay coefficient of 0.0, concentrations at distances corresponding to the downgradient positions of the wells listed on Table 1 can be calculated as a function of time.

Predicted concentrations at the three well locations (assuming the wells lie directly along the plume centerline) after 5,000 days (13.7 years) since source introduction are shown on Figure Attach A-2. In this case, straight lines drawn through the simulated data yield for various dispersivities produce slopes ranging from 0.021 to 0.028, with R^2 values ranging from 0.958 to 1.0, implying decay coefficients on the order of 0.04% to 0.05% day^{-1} . However, in these scenarios, the contaminant is completely conservative. Thus, the inferred degradation rates are false.

This example clearly illustrates the potential for misinterpretation of contaminant degradation by the Buscheck and Alcantar (1995) method even under ideal conditions. In reality, many other factors will distort observed concentration profiles in comparison to those predicted by idealized models. A partial list includes (1) the assumption of steady-state conditions where none exist, (2) fluctuations in source strength with time, (3) non-Fickian dispersion of solutes, (4) strongly heterogeneous flow and transport, (5) placement of wells off plume centerline, (6) dilution effects due to well screen length, and (7) non-uniform degradation rate distribution. Thus, fitting concentration data with an exponential function is perhaps simply a matter of chance in many situations, particularly when few monitoring points are utilized, and thus may provide little real insight into transformation processes.

The sensitivity of degradation rate estimates yielded by Eq. (1) to parameter assumptions also suggests that hydrologic factors, rather than chemical factors, tend to have the greatest influence in this analysis. A sensitivity study, using a Monte Carlo analysis with the input values listed on Table 2, indicates that groundwater velocity and retardation, which are parameters with large uncertainty at LUFT sites, together contribute to approximately 95% of the variance in the predicted degradation rate. On the other hand, Eq. (1) appears to be highly insensitive to several other parameters, among them source concentration, downgradient concentration, the distance between the source and downgradient measurement point, and the dispersivity. The resultant distribution of degradation rates is lognormal, with an order-of-magnitude of variation. The mean degradation rate derived was 0.022%/day, with a standard deviation of 0.013%/day. The associated cumulative distribution is shown on Figure Attach A-3.

Table 2. Input parameters and their distribution

| Parameter | Value - mean (standard deviation) | Distribution | Contribution to variance |
|------------------------------------|--------------------------------------|--------------|-----------------------------|
| Source concentration | 67,000 (67000) ppb | Normal | < 1% |
| Downgradient well concentration | 4095 (409.5) ppb | Normal | < 1% |
| Distance to well | 30-40 m | Rectangular | 1.5% |
| Retardation coefficient | 4 (1.6) | Lognormal | 48.6% |
| Groundwater velocity | 0.029 (0.011) m/day | Lognormal | 46.3% |
| Dispersivity multiplier | 10 (2) % | Normal | < 1% |

In solving the inverse problem for contaminant degradation rates, there are more specific methods available to check that estimates are consistent with field observations. One method is assess whether or not the estimated degradation rate can reproduce the observed generation of geochemical indicators of biodegradation (McNab and Dooher, 1996). An alternative approach is to examine the individual monitoring well average concentrations over time and compare these results to the overall plume length and its temporal behavior (Buscheck et al., 1996).

References

- Buscheck, T. E., and C. M. Alcantar. 1995. Regression techniques and analytical solutions to demonstrate intrinsic bioremediation. Proceedings of the 1995 Battelle International Symposium on In Situ and On-Site Bioreclamation, April 1995.
- Buscheck, T. E., D. C. Wickland, and D. L. Kuehne. 1996. Multiple lines of evidence to demonstrate natural attenuation of petroleum hydrocarbons. Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater. Houston, TX, November 13-15, 1996. National Ground Water Association/API.
- Domenico, P. A. 1987. An analytical model for multidimensional transport of a decaying contaminant species. *Journal of Hydrology*. v. 91, pp. 49-58.
- McNab, W. W., and B. P. Dooher. 1996. Uncertainty analyses of fuel hydrocarbon bioattenuation signatures in groundwater by probabilistic modeling. Submitted to *Ground Water*, December 1996. UCRL-JC-126015, Lawrence Livermore National Laboratory, Livermore, CA.

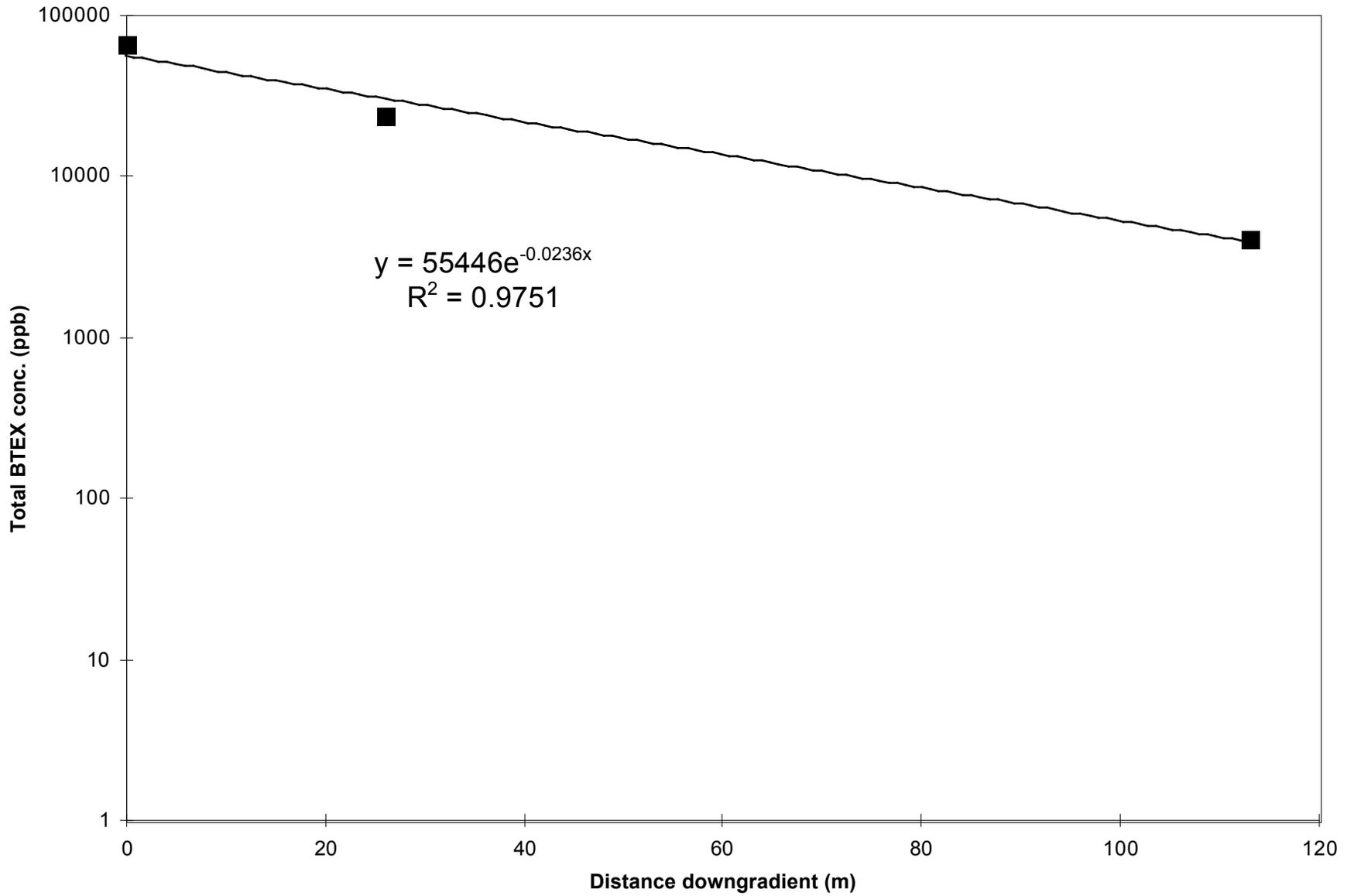


Figure Attach A-1. Concentration versus distance downgradient (site data) used by the method of Buscheck and Alcantar (1995).

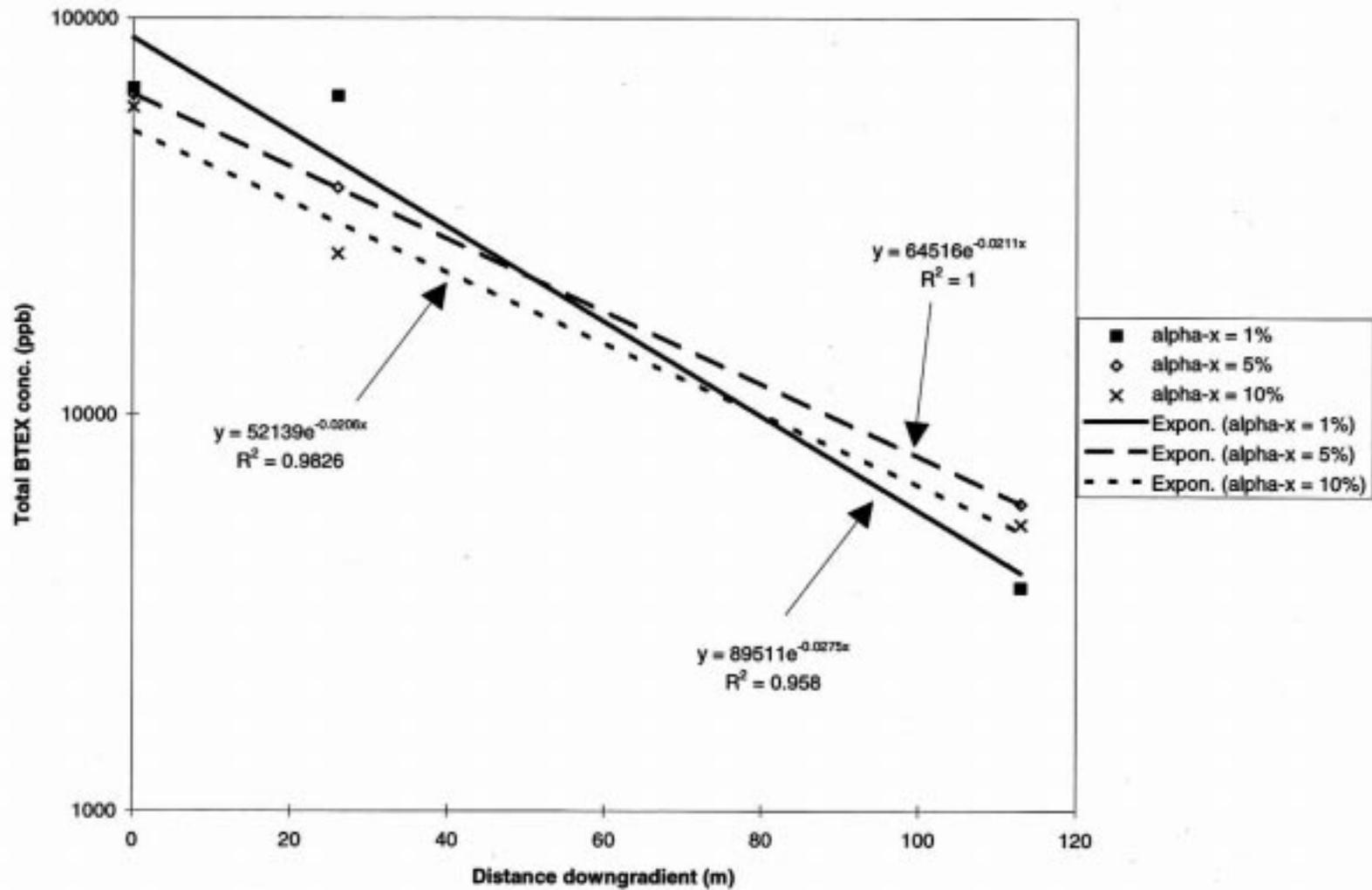


Figure Attach A-2. Idealized Domenico (1987) model of concentration versus distance downgradient from source without degradation.

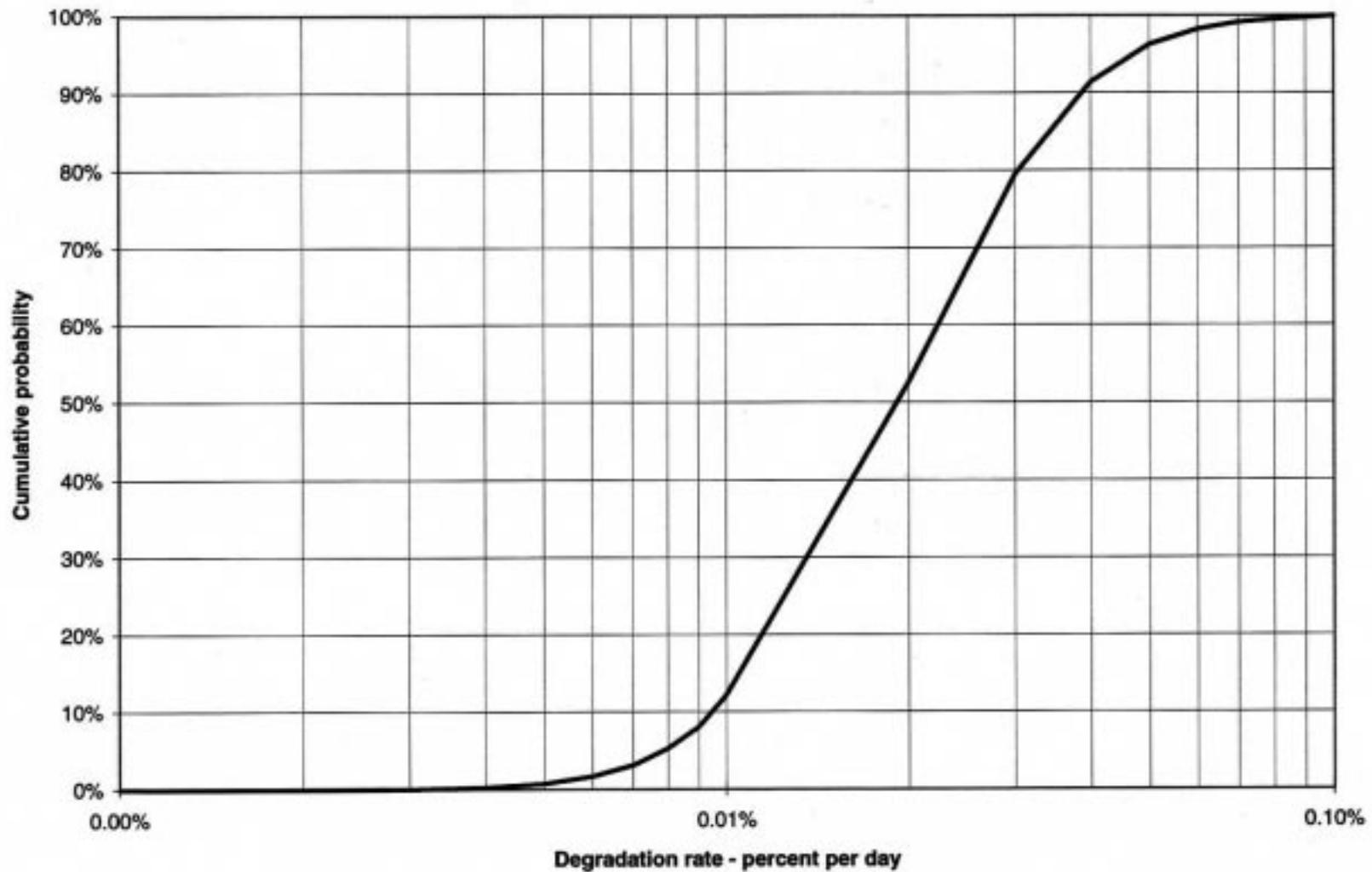


Figure Attach A-3. Cumulative distribution of BTEX degradation rates resulting from Monte Carlo analysis of Eq. (1).